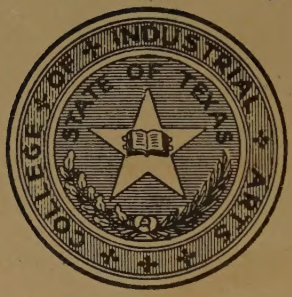

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THE PIGMENTS AND MEDIUMS OF THE OLD MASTERS

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Plate I. Picture Painted about 1600, from the Collection of the late Mr. Hamilton Bruce.

THE PIGMENTS AND MEDIUMS OF THE OLD MASTERS

With a Special Chapter on the Microphotographic Study of Brushwork

BY

A. P. LAURIE, M.A., D.Sc.

Principal of the Heriot-Watt College, Edinburgh
Professor of Chemistry to the Royal Academy, London

WITH THIRTY-FOUR PLATES

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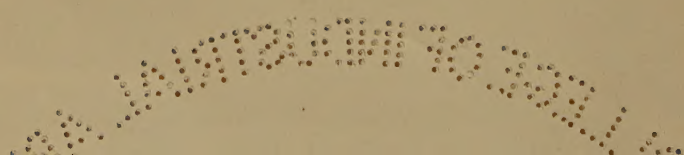


TO

SIR EDWARD JOHN POYNTER, BART.
K.C.V.O., D.C.L., LITT.D.

PRESIDENT OF THE ROYAL ACADEMY OF ARTS

THIS BOOK IS BY PERMISSION DEDICATED

PREFACE

In my former book "Materials of the Painter's Craft," I attempted to bring together in a fairly concise form the amount of information available for a history of the materials used by the artist at various times for painting. In the course of writing the book, I was impressed by the fact that there was a want of exact knowledge on this subject owing to so little experimental work having been done with the view of definitely determining the pigments used at different times. I therefore decided to carry out fresh researches in this direction.

These researches were undertaken with a definite practical object. It seemed to me that a more exact knowledge of the pigments and mediums used at various dates in the history of art, along with methods of identification which could be carried out without injury to the painted surface, would prove of practical value in fixing the dates of works of art and detecting forgeries.

During the enquiry, I was led into an additional branch of investigation, viz., a study of the information to be obtained by microphotographs of portions of

pictures with the view of revealing the brushwork of the artist. The enquiry into the study of brushwork is obviously connected directly with the main purpose of the whole investigation. The two parts of the investigation, the identification of pigments and the study of brushwork, may be regarded as mutually assisting each other. The results of these researches are described in this book.

In conclusion, I have specially to thank Mr. Herbert of the British Museum, Mr. Caw of the National Galleries of Scotland, and Mr. McLintock, Mineralogist in the Royal Scottish Museum, for the invaluable assistance they have given me. In addition, my thanks are due to Dr. Maitland, Mr. Miles and Mr. King, of the Heriot-Watt College, for assistance, and to Professor Eggeling of Edinburgh University Library, Mr. Dickson of the Advocates' Library, Dr. Shaw and the authorities at the Record Office, and the authorities at the British Museum and the Royal Scottish Museum, and the National Galleries of London and Edinburgh, and Dr. Bredius and the authorities at Amsterdam and the Hague, for facilities to pursue my researches.

CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

THE PIGMENTS AND MEDIUMS OF THE OLD MASTERS

THE PIGMENTS AND MEDIUMS OF THE OLD MASTERS

CHAPTER I.

INTRODUCTORY.

The object of the researches which are recorded in this book has been to clear up various obscure points in the known history of pigments and mediums, and by the use of the resources of modern science to obtain direct experimental evidence on the subjects discussed. With this end in view, methods have been devised for the examination of a picture which assist in determining the date when it was painted and in deciding who was the author of the work.

While the ultimate judgment of the value of a work of art must necessarily lie with the art expert, yet there is much that can be done by scientific methods to give him certain definite facts and so narrow the field of his enquiry and enable him to concentrate his judgment on a particular point.

These researches, then, were undertaken with that object in view; but at the same time they have resulted

in supplying a great deal of information which was not formerly known, as to the pigments and vehicles used at different times.

The chemist has been too little appealed to in the past. Where he has been employed, the result has always been the supplying of exact and valuable information, but he has not been encouraged to make a systematic enquiry through the centuries. Moreover, he has not been called upon to devise methods of enquiry which, while sufficiently exact, would not involve injury to the object examined. No doubt a dread of his methods has been the reason why he has not been employed.

Yet, such is the inconsistency of the owners of pictures, that, while the chemist has been warned off, priceless works of art have been handed over in many cases to ignorant and reckless picture restorers, with disastrous consequences.

As the object of this book is to describe the results of direct experiment, it is not proposed to quote at length the results already obtained by a purely literary enquiry into historical documents. All that can be done in this connection has been done by previous writers, and for such purposes it is only necessary to consult Eastlake and Mrs. Merrifield among the earlier authors, or Mrs. Herringham and Professor Ernst Berger among the later authors, to learn all that is known or conjectured by these methods. No doubt the most valuable contribution to these subjects has been made by Ernst Berger in his "Beiträge zur Entwickelungs-Geschichte der Maltechnik." He has collected in that work the results of exhaustive research

into all known sources of information, combined with many ingenious experiments and suggestions. Professor Ernst Berger has developed very definite views on many of the problems at issue. It should be remembered therefore in reading his invaluable work that he is in many cases developing the arguments for a certain conclusion, and that other authorities may take another point of view from that adopted and argued for by the Professor. If this is done, his books will be found to be full of useful information.

The author in his own books "Greek and Roman Methods of Painting" and "Materials of the Painter's Craft," has done his best to sum up the information on this subject without any undue bias in favour of special theories, and has supplied a very full bibliography.

It is unnecessary to repeat the information contained in these works, and therefore, in the present volume, references to literary sources of information will only be made when necessary for the development of the argument.

At the same time, it seemed advisable to sum up in a table the information as to the history of pigments available from these sources. This table will presently be discussed. It has the fault of all summaries in that it is apt to be too dogmatic. It is only meant to be a a basis for reference, and where matters are in doubt, the author has filled in a date to the best of his judgment as probably the most reliable.

Later, the results of actual experiments are given—results which do much to develop and correct this table.

Before however discussing the table, it is necessary

to describe the methods that have been employed. Beginning with the literary information, the first step in the enquiry was to prepare and examine the various pigments that have been used in the history of painting. These pigments were examined under the microscope, and where such methods were available, they were also examined with polarised light; and simple chemical tests for identification under the microscope were devised. Provided with this information, the next step was to examine works of art of known date with the view of identifying these pigments and searching for others.

For this purpose, the illuminated manuscripts provide the best material for several reasons. In the first place, the dates of these are in many cases exactly, and in other cases approximately, known. In the second place, these documents may be relied upon as genuine. No forger has apparently had the courage to attempt to reproduce an illuminated missal from end to end, nor, with very rare exceptions, have they suffered at the hands of the restorer. In the third place, the pigments are laid on pure with little medium, and therefore their identification is rendered comparatively easy. In the fourth place, the brilliant pigments used are those of most interest to us in the present enquiry. This requires explanation.

There are many pigments, such as the earth colours (red and yellow ochres), bone black and lamp black, white lead and chalk, which have been on the artist's palette from classical times, and therefore are of little interest in this enquiry. But there are more brilliant pigments which have disappeared and others which

have been added, and these deserve our special attention.

By means of these manuscripts, it is possible to trace the history of pigments from the seventh to the close of the fifteenth century. After that such documents begin to become rare, but fortunately there exists another series of dated documents which are available —the Court Rolls in the Record Office. It was customary to adorn the first page of these with gilt letters and a miniature from about 1500 to about 1700. Therefore, these dated and untouched documents carry our information up to 1700; and in addition we have the Venetian Ducali. I have in my possession a parchment appointing a Captain of the Inquisition dated 1719, which brings the record a little further, as it is adorned with painting.

It may be objected that the pigments used on the manuscripts do not exhaust the possible pigments used at different times. This is no doubt true, but at any rate they supply definite direct information which can be added to by further research from time to time.

In the following pages will be given the results of this enquiry into the pigments used by the illuminator.

In the case of pictures, the enquiry is more difficult, especially when oil is the medium, as the particles are so smothered in oil as to be with difficulty recognisable.

The actual methods employed in examining the surface and in removing microscopical samples when permitted will be described in a subsequent chapter.

The extent to which the information obtained by

these methods is trustworthy varies considerably. In most cases it is absolutely trustworthy but sometimes, either because of difficulties put in the way of an exhaustive examination, or because of special circumstances making it impossible to employ exact methods of identification, the results obtained must be regarded as having a high degree of probability rather than as being absolutely certain. In the course of this book, wherever these points occur, care has been taken to use language which will indicate the extent to which the conclusions arrived at can be taken as absolutely certain or merely highly probable.

In addition to the exact study of pigments and mediums, another method of enquiry is described in this book, namely the study of brushwork by means of the "micro-camera."

While engaged in examining pictures in the ways described, I was impressed by the fact that when magnified in a suitable way, a picture often revealed the brushwork of the artist in a remarkable manner. In the case of pictures in which tiny figures were painted, such as those by Watteau, or in the case of landscape pictures, the magnification of the surface brought out at once the subtle painting and modelling of the artist, which was invisible to the eye, in a remarkably characteristic manner. The treatment of foliage, for example, reveals in every case the peculiar methods of the master.

In the case of larger pictures, the application of the method is more difficult and the best results are obtained by photographing the eye in the case of life-sized portraits. In order to obtain in this way

authentic records of the brushwork of various artists, it was necessary to devise a special camera—the instrument may be described as something between an ordinary photographic camera and a microscope—and by it to obtain a direct enlargement of a small portion of the picture on the negative. In this way I am gradually compiling a complete dossier of leading artists for reference, which will be of great value in detecting copies, forgeries, and the work of pupils.

Two methods are available, therefore, for identifying and dating a picture, namely the study of the pigments and mediums used, and the study of the brushwork by means of the micro-camera.

In this book the pigments known in the time of Pliny are taken as the datum line, and it does not contain any systematic investigation into Egyptian pigments. It is evident, however, that a similar systematic enquiry should be made into Egyptian pigments. It is customary to speak of pigments as being used in Egypt without any definition of the dates, thus causing much confusion. Such an arrangement according to dates could easily be made.

CHAPTER II.

TABLE OF PIGMENTS PREPARED FROM LITERARY SOURCES.

As explained in the opening chapter, the table at the end of this chapter is entirely compiled from information obtained from literary sources, without in any way making use of the material obtained by the actual examination of dated documents. It will be found, however, that the table is most useful if left in this form, so as to make it possible to refer back constantly to it as fresh and more exact information is collected from the examination of illuminated manuscripts and pictures.

The pigments at the head of the table are those known in the time of Pliny. Space need not be occupied by discussing this list or by giving the references necessary in order to prove the correctness of the statements it contains. These have already been dealt with so fully in other books, that they do not require repetition.

In addition to the actual pigments mentioned here, there are certain other references to pigments in Pliny which are very obscure, and difficult of interpretation.

I do not propose, therefore, to load the table with any guesses or discussion of these, merely dealing with those about which we have positive information.

Let us begin by discussing the pigments known in the time of Pliny which are printed along the top of the table. In the first column will be found the blues.

Indigo.—There can be no doubt from Pliny's description that both varieties of indigo were known; that is to say, the indigo obtained from the dyers' vats in which woad was prepared, and the indigo from India.

Egyptian Blue.—This double silicate of copper and calcium was manufactured in Egypt, and according to Vitruvius also in Puttioli by Vestorius. It was used universally throughout the Roman Empire, but its manufacture seems to have ceased by the seventh century. At the beginning of the chapter on Byzantine Manuscripts the question as to whether Egyptian blue was ever used after Classical times is discussed fully.

Azurite.—This is the native blue carbonate of copper. It seems to be referred to in the time of Pliny as Lapis Armenius, and also probably in some cases as Cyanos and as Sapphiros, azurite being probably confused with lapis lazuli in certain cases.

Red Ochre.—Under the head of reds, there are to be found the ordinary red ochres which require no further description.

Red Lead.—The preparation of this pigment clearly described by Pliny, is by roasting white lead, and it has been found upon Roman frescoes.

Cinnabar.—The method of preparing mercury from its ores was known in the time of Pliny, but no receipt

is given for the preparation of artificial vermilion by subliming together mercury and sulphur. At the same time, cinnabar is clearly described as a pigment.

Dragon's blood.—This is described clearly by Pliny, who gives an amusing account of its origin, and describes it as an import from India.

Madder, kermes.—Both these dyes are mentioned as materials for the preparation of lakes, but these lakes differ somewhat from what is meant by a lake to-day and in mediæval times, as the dye was precipitated upon chalk or gypsum, thus forming a more opaque pigment differing from the transparent lakes on an alumina base. Madder lake prepared on these lines has been identified by the late Prof. Russell in some Egyptian pigments. Other vegetable reds were evidently used also, judging from Pliny's description.

Yellow Ochre.—Under the head of yellow, we have of course the natural yellow earth known as yellow ochre.

Oxide of Lead.—The preparation of the oxides of lead, massicot and litharge, are clearly described by Pliny; and I have found massicot of fine quality in what is known as the Scribe's palette, supposed to be about 400 B.C., which is in the Museum in Edinburgh.

Orpiment.—Another yellow described by Pliny is orpiment—the yellow sulphide of arsenic. He also describes realgar.

Vegetable Yellows.—There are various vegetable yellows and yellow dyes, such as weld and Persian berries and Quercitron bark, referred to, materials which are still used for the preparation of yellow lakes such as "Dutch Pink."

Malachite.—Under greens we have malachite, the native green carbonate of copper.

Verdigris.—A clear description is given of the preparation of verdigris by the corrosion of copper plates from fermenting grape skins.

Terre verte.—This green earth has been identified on the Roman frescoes.

Green vegetable pigments.—The modern form of these is known as sap green.

Under whites, we have references to *chalk*, *gypsum*, *white lead*, and apparently other white earths with which we need not be concerned here.

Under black we have *black chalk*, *lamp black* and *bone black*, all described clearly.

Tyrian Purple.—Under purples, we have the description given both by Pliny and Vitruvius of how to prepare a pigment from the Tyrian purple; and there are also receipts apparently for preparing vegetable purples.

We now begin to move down through the table. The first date of importance is the receipt for making *artificial vermilion* in the manuscript in the cathedral library at Lucca which is of about the eighth century.

Lac Lake.—The next definite date for the introduction of a new pigment is the importation of Indian lake. The use of the word "lac" on early manuscripts seems to apply indefinitely to the juice of the ivy, which was apparently used as a transparent red pigment, and Indian lac. According to Mrs. Merrifield (Vol. I. p. clxxvii, collected from the Statutes of Marseilles which are cited by Depping), Indian lac was imported in 1220 by the Catalans and Provençals for

the purpose of dyeing. From this time, therefore, we should expect to find lac lake used for painting purposes.

The next definite description of new pigments is to be found in thirteenth and fourteenth century manuscripts, more especially in the manuscripts of Jehan le Begue who, while himself living in the fifteenth century, had collected older manuscripts; and they are to be found in the first volume of Mrs. Merrifield and elsewhere.

Ultramarine.—In these manuscripts we first find definite receipts for the preparation of real ultramarine from lapis lazuli.

Sapan Wood.—We also find references to lakes prepared from Sapan wood imported from Ceylon.

Naples Yellow.—The first reference to Naples yellow is to be found in Cennino Cennini, and he there speaks of it as a native volcanic pigment, but in the Bolognese manuscript of a slightly later date, it is described as an artificial preparation of lead and antimony oxide. I think therefore it is very doubtful if Cennino Cennini was right in supposing that Naples yellow was a volcanic pigment; it is still used in connection with the glazing of pottery.

Cochineal.—After the Conquest of Mexico, in 1523, cochineal was introduced, and lakes prepared from it were first described by Matthioli in 1549.

Smalt.—This is a blue pigment which is prepared by making a deep-coloured cobalt glass; and it has been known both as Smalt and Zaffre in the history of painting. There is some obscurity as to when it was first introduced, as the word "smalto" is used as early

as 1492 by Leonardo da Vinci in referring to the decoration of the apartments in the castle of Ludovico il Moro. It is fairly evident from Lomazzo and from the Marciana Manuscript "Ancient Practice of Painting," Mrs. Merrifield (Vol. I. p. ccvii, Vol. II. p. 616) that the word "smalt" was used to describe the vitrified pigments used for painting on glass, and was not at first confined necessarily to blue. It is very highly probable that among these pigments there would be blues, though these blues might be either obtained by colouring glass with copper, or with cobalt. The matter has been further confused by the impression that the old Egyptian blue was also known in the fifteenth and sixteenth centuries, though I have not been able to find any definite evidence of this. This false impression has been confirmed by a receipt for the preparation of Egyptian blue being given in the Brussels Manuscript (page 804, Mrs. Merrifield), and written by Pierre le Brun, the painter. When, however, this receipt is examined, it is found to be an almost exact translation from Vitruvius, and therefore is no indication that the preparation of this blue was understood at this time.

There seem to be only two perfectly definite references to what we now know as Smalt—that is a blue cobalt glass of sufficient pigmentary depth to be able to be used in painting, which can be taken as helping to fix the date of its first introduction.

Borghini in his Il Riposo mentions Azzurro di Smalto, and states that it is a glass. Here we have the two words "Smalt" and "Blue" associated with each other. The second reference is to be found in a historical work on the Mines in Misnia written by Christian

Lehmann (1688), and quoted in Beckmann's "History of Inventions," Vol. I, of Bohn's translation. According to Christian Lehmann, the blue was invented by Christopher Schürer, a glass maker of Platen, and he states that at his time the factories for making the blue were about one hundred years old. We must assume, then, until we have further evidence, that smalt was introduced in the latter half of the sixteenth century, and was not known at an earlier date.

Prussian Blue.—The next pigment we come to in our list is Prussian blue, which was discovered by Diesbach, a dyer, and the date of his discovery is variously given from 1704 to 1720.

The remaining pigments may all be said to belong to modern times, and to be due to the birth of modern chemistry towards the close of the eighteenth century. Here the dates given are either from the actual discovery of a compound by some well-known chemist, or from the earliest date at which I have been able to find a record of its sale in the lists of artists' colourmen. Where the date is that of the first discovery, of course the actual use of the pigment would come a little later, but many of these new pigments seem to have come very early on to the artist's palette. In finding out the exact date when a pigment has first been sold to the public, I have been very much assisted by Messrs. Newman, Reeves, Winsor & Newton, and Roberson, who, by turning up their old catalogues, have been able to say definitely when a pigment was first introduced to the public; and I wish to take this opportunity of thanking them for their courtesy in the matter.

Verditer.—It will be noted that at the bottom of the table under the head of Blue there is a reference to the artificial carbonates of copper. This reference might be introduced under the head of green, as we find in the eighteenth century palette two artificial copper carbonates known as Blue and Green Verditer, which are still to be obtained from artists' colourmen. It is quite impossible from historical evidence to decide when these artificial copper carbonates were first introduced.

The receipts for the preparation of such artificial azures are very old, some workable, and some absurd. De Mayerne, however, seems quite clearly to describe two copper blues, viz., the natural azurite, and an artificial blue. These copper blues were known as blue ashes, mountain blue, bice, and verditer, and it is quite impossible to decide definitely when the natural carbonate was replaced by the artificial under these names, the only definite piece of information being the apparent reference to both by De Mayerne, but it is, of course, not perfectly certain that he was right in saying that one of these blues was an artificial product, although he was under that impression.

TABLE OF PIGMENTS

	BLUE	RED	YELLOW
Pigments known in the time of Pliny.	Indigo. Egyptian Blue. Azurite.	Red Ochres. ,, Lead. Cinnabar. Dragon's Blood. Madder } Lakes. Kermes } Other vegetable reds.	Yellow Ochre. ,, Lead Oxide. Orpiment. And vegetable pigments.
Lucca MS., 9th cent., 1220.		Artificial Vermilion. Lac imported.	
First described in 13th and 14th century MSS.	Real Ultramarine.	Lakes from Sapan wood.	
Cennino Cennini, early 15th century. Bolognese MS., 15th century.			Naples Yellow. Artificial Lead, Antimony Oxide. Later still, imitation of this.
Conquest of Mexico, 1523. First described by Matthioli, 1549.		Cochineal Lakes.	
First definitely described by Borghini, 1584.	Smalt.		
Discovered by Diesbach, 1704–1720. 1778. 1781. 1797.	Prussian Blue.		Chrome Yellow.
1804. 1820–30. French Government Prize, 1828. 1835.	Cobalt Blue. Artificial Ultramarine.		
1846 (1851 Exhibition).			Cadmium Yellow.
1861. 1862. 1870.	Cerulean Blue.		Aureoline, or Cobalt yellow.
	Blue Ashes, Bice, Verditer in 18th century. These were artificial copper carbonates and hydrates. When they replaced native carbonates unknown. The receipts very old.	The first use of Lakes from Indian Lac doubtful, as a red from Ivy Gum had the same name.	

FROM LITERARY SOURCES.

GREEN	WHITE	BLACK	PURPLE
Malachite. Verdigris. Terre Verte. Green vegetable pigments.	Chalk. Gypsum. White Lead.	Black Chalk. Charcoal. Lamp Black. Bone Black.	Tyrian Purple from the Murex. Prepared by Irish monks from Carpillus Purpura. Vegetable Purples.
Scheels Green.	Zinc White.		
Emerald Green. Cobalt Green.			
Oxide of Chromium [Greens.			

CHAPTER III.

THE METHODS OF EXAMINATION OF THE PAINTED SURFACE BY MEANS OF THE MICROSCOPE. REMOVAL OF MICROSCOPIC SAMPLES, AND THE APPLICATION TO THEM OF OPTICAL AND CHEMICAL TESTS.

In the course of carrying out these examinations, various pieces of apparatus and methods have been devised. In the first place, it is necessary to have a microscope which is mounted on a rod with rack and pinion, so as to be able to travel to and fro. For this purpose an ordinary cathetometer stand to which the microscope is attached is very convenient, the cathetometer stand being so arranged that it can be used either horizontally or in a perpendicular position.

The most useful magnification is about 100 diameters, which is sufficient to resolve the coarsely ground pigments used in the past into their separate particles, while at the same time it is not too near the surface of the picture or manuscript to prevent illumination from the side. Methods of illumination by the introduction

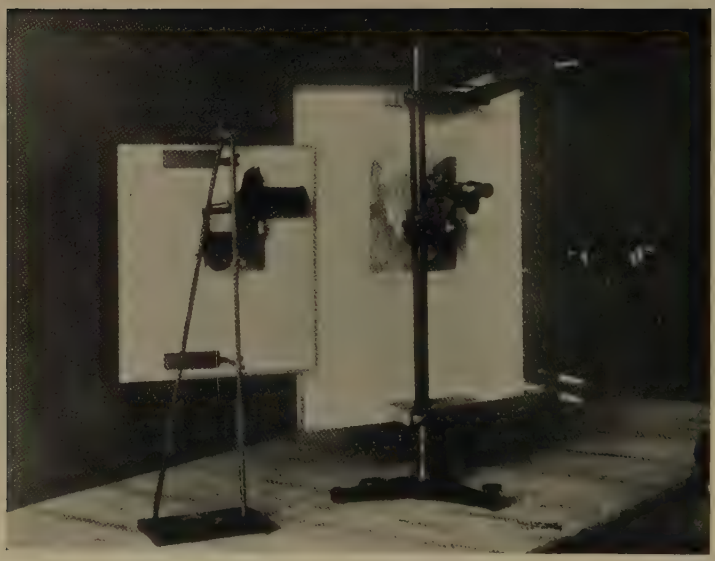


Plate II. Examination of a Picture with the Microscope.

of a mirror into the tube of the microscope are not very satisfactory, and it is better therefore when a higher power than this is required to do it by altering the eye-piece and leaving the object glass the same, but for most purposes a No. 3 eye-piece is quite sufficient along with the object glass already described. Where necessary, it is easy by means of a lens to concentrate daylight, or to make use of artificial light from a Nernst lamp or small arc. On the whole, artificial light is not to be recommended, as it is much more difficult to distinguish the colours of the pigments with such light, than by ordinary daylight; if the object is placed in a well-lighted window, concentration by means of a lens is usually unnecessary.

For purposes of comparison, it is necessary to have all the pigments which are likely to be found prepared and painted out with a little gum on tiny squares of paper. These can be placed under the microscope, and the microscope adjusted so that part of the field is covered by the pigments for comparison.

For the purposes of taking samples, two or three instruments will be found useful. In the first place, for removing tiny samples of pigments without producing any injury to the surface, the most useful instrument is a hypodermic needle, but an ordinary hypodermic needle is rather too long and elastic. It is better therefore to cut it down so that it is only some three-eighths of an inch to half an inch in length, and then grind the point as before. When a sharpened needle of this kind is dipped in Canada Balsam of the usual dilution, and then allowed to dry for a few minutes in the air, the surface becomes sticky, so that

if the point is just touched against the surface of the pigment, a tiny particle will be removed and remain sticking to the point of the needle. The only other thing necessary is a glass slide with a drop of Xylol upon it. The point of the needle is pressed into the drop, and in a few minutes the Xylol will evaporate, leaving the particles attached to the glass and ready for examination.

While taking a sample, it is necessary to magnify the surface, and the most useful arrangement for this purpose is a pair of Zeiss' stereoscopic magnifying glasses which are fitted with an elastic band so as to leave both hands free for manipulation.

For taking coarser samples, a very convenient instrument is a tiny steel gouge attached to a metal handle of the kind used for dentists' instruments, the gouge itself being slightly curved upwards. This gouge should not be more than a millimetre in diameter. It is easy to separate a sample with this, and then by slightly moistening the back of the gouge, to pick it up and remove it to an object glass. In some cases the object glass can be smeared with a fine layer of Canada Balsam in order to attach the particle, or with a little collodion mixed with castor oil. In some cases, where any such medium is objectionable, the particle is best placed on a glass slide in which a slight depression has been ground so as to enable the reagent with which the particle is to be attacked to be added in sufficient quantity, thus forming a shallow evaporating dish.

Where it is required to take a sample through a picture, the best instrument is a hypodermic needle

Plate III.

APPARATUS FOR SAMPLING PICTURES.

ACTUAL SIZE.

which has been ground and sharpened so as to form a miniature cork borer. A fine steel wire is then fitted with a handle so that it can be pushed through the cord borer and so force out the required sample. In this way circular borings can be taken through the whole of a picture for examination. Such borings are best mounted in paraffin wax so as to enable them to be cut into sections, and for this purpose the most convenient arrangement is to have a series of little glass tubes about three-eighths of an inch in diameter by half an inch long which are closed at the bottom by means of corks. The glass tube is filled up with paraffin wax, which is then easily pushed out, and the top of the little cylinder shaved off so as to be perfectly flat. A tiny groove is then made in the top of the paraffin wax, and the steel wire carefully pushed into the miniature cork borer. The result will be to push out the sample which will remain attached to the end of the cork borer. It is then carefully laid in the little groove in the paraffin wax cylinder either upright or otherwise, according to the direction in which the sections require to be cut. With a stout platinum wire, a little paraffin wax is then melted on to and over the section, and it is only necessary to attach the bottom of the cylinder to an ordinary section-cutter and then proceed to cut sections with a razor.

These sections are placed on a glass slide, the rough of the paraffin wax melted off, and the section finally cleaned up with Xylol. If care is taken, the section will still remain attached to the glass and is then ready for examination. Even if the picture has been painted

in oil there is no difficulty in attacking such sections with chemical reagents, while the oil forms a convenient medium to hold the material together while it is being attacked. Sometimes it is necessary to examine the cylinder itself before cutting sections through it. This is easily done by placing the paraffin block under the microscope, and if the eye-piece has introduced into it one of the usual arrangements for measuring purposes, it is quite easy to measure the thickness of the different layers of paint, gesso, and so on before proceeding to cut up the section for further examination. In a large number of cases the microscopical examination of the section gives all the information required.

After this examination, one can proceed in some cases to examine with a mineralogist's microscope through crossed nicols, or to apply various reagents by putting a drop upon the slide. In many cases, in order to start the attack, slight warming is necessary, and for this purpose there is nothing more convenient than the top of an ordinary water bath oven which is sufficiently warm to start the reaction without over heating the particle of pigment.

In some cases it is best to evaporate to dryness and then examine the residue. If it is necessary to stain the section, this is readily done in the usual way by immersing in a bath of the required stain.

In a great many cases the obvious tests to be applied would occur to any chemist, but the principle to be followed in selecting a suitable reaction is that the change should take place upon the particle of pigment itself. In this way reactions become very sensitive, and

the minutest particle is very often quite sufficient for purposes of identification. It is seldom necessary to employ more than one reaction, as the possibilities as to the special pigment are limited; its appearance has already probably been sufficient to identify it, and one decisive reaction will settle its composition.

Where the action of the reagent is apt to be rather violent; for instance, if it is necessary to use a strong acid such as nitric acid or hydrochloric acid, it is often advisable to cover the particle of pigment with a thin film of collodion, and then apply the reagent over the collodion, when it will diffuse through and act upon the particle of pigment without immediately dissolving or destroying it, while the presence of the collodion concentrates the reaction in the neighbourhood of the particle of pigment. For instance, in acting upon lakes with nitric acid, or in applying Reinsch's test to an arsenic green, this protection with a film of collodion will be found essential.

Reference has already been made to the polarising microscope. It is quite essential to have a good mineralogist's microscope as it is often necessary to make an exhaustive optical examination of the particles of pigment.

If oil of Cassia is used to mount the fragment, it will be found that blue and green verditer and verdigris have refractive indices below that of oil of Cassia, while azurite and malachite have refractive indices above, and can thus at once be distinguished.

Where it is necessary to do a separation, the reagent can be added to the solution on the slightly hollowed glass slide, the whole solution concentrated, the little

drop of liquid soaked up by a tiny piece of filter paper, which is then dried and moistened with the reagent required for the second test.

Tiny quartz vessels some two or three millimetres in diameter with quartz rod handles are also useful, and many other methods will be found in books on micro-chemistry.

CHAPTER IV.

ON THE PROPERTIES AND REACTIONS OF CERTAIN PIGMENTS WHICH ARE OF IMPORTANCE IN THE HISTORY OF ART.

In Chapter II, the history of pigments in so far as it can be derived from literary sources has been briefly summarised. In later chapters the history of pigments roughly from the 7th to the end of the 18th century will be dealt with, in so far as information can be derived by the actual examination of known dated documents and pictures, and, as already explained, only those pigments will be considered which are of interest because they are easily identified and because they appear and disappear in the course of the history of painting. A similar investigation might equally well be made into the pigments used in Egypt, with the view of fixing dates, as no doubt changes of the palette occurred there just as elsewhere. I have not had the opportunity so far of making such a study of Egyptian pigments, and am confining myself to the pigments used in Europe and Byzantium during the period already mentioned.

The pigments, therefore, which will now be described will be in the first place those found on illuminated manuscripts; and they will be dealt with in detail. In addition, a short description will be given of such pigments, both ancient and modern, as are of importance from the point of view of our present enquiry, with a description of methods of recognising them when obtained in microscopic samples, and more especially when mixed with an oil medium.

It must be understood that in giving the descriptions of the pigments which follow, there is no pretence of providing a complete account of the exhaustive chemical tests which may be applied for their identification. These can be found in ordinary works of analysis. The descriptions that follow are written from the point of view of the identification of pigments on manuscripts and pictures, where they have either been examined *in situ* or in fragments suitable for microscopic examination; and therefore such tests are selected as have been found useful for examination under these conditions. Any chemist can confirm these where it may be necessary by using recognised analytical methods.

Gold.— The metal gold is used in decorative art in three forms. The first of these is gold leaf, in which metallic gold is beaten out in thin sheets. There is no need to describe the process here: it is very old, and is described by Pliny. Pliny states that gold leaf should be laid on by means of white of egg; and what is known as water gilding is usually done with white of egg or slightly putrid size. The processes used to-day are the same as those described

by Cennino Cennini for raised gold ornaments. First of all a preparation of Gesso is made consisting of chalk and parchment glue. This having been smoothed, is laid over with a fine coat of bole which is a soft clayey variety of red ochre mixed with a little of the parchment glue or white of egg, and the gold leaf is then laid upon the surface of bole with the white of egg, and is polished with an agate or dog's tooth.

The other method of laying gold is by means of gold size, which is a preparation of linseed oil and varnish and lead dryers boiled into a thick consistency. Receipts for the preparation of modern gold size will be found in books on pigments and varnishes, and probably differ very little from the descriptions of methods of preparing it in the past. A description of the preparation of gold size of this nature is given by Cennino Cennini. (Page 151, Mrs. Herringham's translation.)

Gold is also used as gold paint, and for this purpose leaf is taken and ground into a powder. The description of how to do this will be found in Chapter 160 by Cennino Cennini (Mrs. Herringham), where he advises the grinding up of gold leaf on a porphyry slab with white of egg. Theophilus describes mortars for the grinding of gold, the description being a little difficult to understand, as it is impossible to grind metallic gold, and he must therefore refer to the grinding of gold leaf or of some alloy of gold which was sufficiently brittle to be treated in this way.

The third use of gold for decorative purposes is

to be found on certain English manuscripts which seem to have been painted with rounded granules of gold which have all the appearance of the gold obtained by the washing of auriferous river sand. These gold granules are laid directly on the parchment without any preparation of gesso and have afterwards been burnished. From its appearance, there can be very little doubt that this gold has been obtained from river washings, and that the only preparation has been to sift out the finer grains from the coarser grains.

Under the microscope, there is no difficulty in identifying gold paint prepared from gold leaf as the little particles are very thin and have sharp corners and edges, differing entirely in appearance from the rounded granules of river washed gold dust.

Vermilion.—Vermilion is the red variety of sulphide of mercury and occurs in painting in two forms—the natural and the artificial. The natural sulphide of mercury is known as cinnabar. It occurs in either crystallised, massive or earthy varieties and is a bright reddish brown in colour. The crystals belong to the rhombohedral system. Cinnabar is found native in various places, the best known European deposits being Almedan in Spain and Idria in Carniola. It is quite easy to obtain specimens of the native cinnabar which on grinding produce a beautiful pigment, differing little from artificial vermilion in brilliancy, but of a more brick red colour. Under the microscope the ground pigment is seen to consist of translucent glowing, deep red particles.

The oldest method of making the artificial vermilion is by subliming together mercury and sulphur in a closed crucible, the vermilion collecting at the top. This is the method described in the Lucca Manuscript; and it is evident from Cennino Cennini that in his time artificial vermilion was the one used. At the present day this method of manufacturing is in use in China. It has been replaced in Europe by wet processes which need not be described here. I have not found any method of distinguishing between cinnabar and artificial vermilion with the microscope. The modern vermilions are much more finely ground, but the coarser lumps have just the same appearance as cinnabar, and the difference in tint, although quite obvious when cinnabar and artificial vermilion are laid side by side, is not sufficiently definite to be trustworthy when examining a painted surface. There is no difficulty in identifying vermilion by matching with the eye against known samples, and then confirming by matching under the microscope. An oil film resists attack by both hydrochloric and nitric acid.

The only pigment with which vermilion might possibly be confused is red lead, but this is quite easily decided by matching with vermilion and red lead samples, and by the fact that red lead has almost always slightly discoloured from the formation of lead sulphide, while should a further distinction be necessary, if the minute fragment under the microscope is moistened with sodium sulphide, the red lead will at once blacken, while the vermilion is unaltered. It was apparently customary, judging from the

receipts, to mix vermilion with red lead in certain cases when painting illuminated letters.

In Pliny vermilion is described as Minium, which is now used to describe compounds of lead.

Red Lead.—Red lead is occasionally found native, and its artificial preparation is clearly described by Pliny by the roasting of white lead. It can be prepared in two ways—either by the careful roasting of lead oxide in a furnace with a large admission of air, this being the way in which it is prepared in large quantities for commercial purposes, or by the roasting of white lead. The product obtained by roasting white lead is rather more orange in shade, and while it is impossible to speak with certainty, the red lead appearing on illuminated manuscripts seems to match better the white lead product. Red lead is easily identified by matching with a known sample under the microscope, and usually also shows certain portions which are not only dark brown or black, but have a curious metallic lustre due to the action of sulphuretted hydrogen gas on the lead. If the particle of red lead be moistened with sodium sulphide or sulphuretted hydrogen water (this acts slowly on oil films), it at once turns black, thus distinguishing it from vermilion and from cadmium orange. Red lead in oil can be further distinguished by the fact that when the particle is treated with strong nitric acid it turns a dirty brown colour owing to the formation of peroxide of lead.

If an orange chrome is treated with nitric acid, it at once becomes bright yellow, while cadmium orange is at once decomposed by the acid with effervescence.

On illuminated manuscripts, no question as to its being red lead can possibly arise, but in the case of oil paintings, it might be confused with orange cadmium or orange chrome.

Orpiment.—Sulphide of arsenic or Orpiment is found in orthorhombic crystals, the surface sometimes appearing entirely crystalline, but also in other cases scaly and fibrous. It is a very brilliant yellow, of a quality of tint which is usually quite unmistakable when matched with a known sample under the microscope, though occasionally owing to the surface having got rubbed, it is not so easy to identify. There also seem to be indications that in some cases it has faded where it has been used on illuminated manuscripts; and the condition of this fading is worthy of further investigation. Orpiment is found native in various parts of the world, among which may be mentioned in Europe, Hungary, Bosnia, Tyrol, Baden, and Civita Vecchia in Italy. It is often found associated with realgar, the orange sulphide of arsenic, which on exposure to light tends to turn into orpiment, so that little orange particles of realgar will sometimes be found mixed with the yellow orpiment.

If moistened with sodium sulphide, it does not blacken, thus distinguishing it from lead compounds, while at the same time it dissolves in sodium sulphide.

This solubility in alkaline solutions can be confirmed by moistening another portion with a drop of caustic potash. The cadmium yellows are not discoloured by sulphide of sodium, but are insoluble both in sulphide of sodium and caustic potash, and are blackened by an acid solution of silver nitrate which does not change

orpiment in oil, but turns pure orpiment dirty grey. It is difficult to distinguish sometimes when rubbed and dulled from a fine French yellow ochre on the surface of a manuscript, but yellow ochre resists the solvents and if necessary can be confirmed as an iron compound by the usual reactions.

The oil film is not attacked either by strong hydrochloric or nitric acid.

Massicot Yellow.—Yellow oxide of lead, massicot. Yellow oxide of lead is obtained by the roasting of metallic lead, or by the heating of white lead. It blackens with sodium sulphide and sulphuretted hydrogen, and is readily dissolved from an oil film by acetic acid, forms a dull yellow and is not used by the modern artist.

Yellow Lake (*Dutch Pink*).—These yellow lakes are prepared from Persian berries or quercitron bark. They dissolve in acetic acid and turn deep orange when treated with caustic potash, and are bleached by chlorine water.

Gamboge (*Garcinia Morella, Habitat*). — Siam, Ceylon. The deep transparent orange of gamboge can usually be recognised on a manuscript directly under the microscope. It is dissolved by acetic acid and turns deep orange red with caustic potash.

Malachite.—Malachite is a basic cupric carbonate and is a native green copper mineral which belongs to the monoclinic system, but is often amorphous and very slightly crystalline. It has a characteristic appearance under the microscope, and differs so much in tint from other greens that it can usually be identified on an illuminated manuscript by

matching. In order to test whether it is a compound of copper, the microscopic particle should be moistened with a slightly acid solution of potassium ferrocyanide, when the red copper ferrocyanide is at once formed, while the effervescence of the particle if moistened with a weak acid proves it to be a carbonate. It is very necessary to be able to distinguish it from artificial copper carbonates such as green verditer. Green verditer is not crystalline, and malachite usually contains, when examined through crossed nicols, a few doubly refracting particles. Moreover, if the pigment is mounted on a microscope slide in Cassia oil (refractive index 1·6) and examined under the microscope with the light stopped down, the white fringe which then appears at the boundary between the oil and the fragment is found to move from the fragment to the oil when the objective is raised, if we are dealing with green verditer, whilst it moves from the oil to the fragment if the latter is malachite. The reason for this is that the refractive index of verditer is well below 1·6 whilst that of malachite is much above that figure (about 1·9).

Verdigris.—The verdigris of the fifteenth century manuscripts consists, at any rate, partially of doubly refracting crystals which are below oil of Cassia in their refractive index, but it is of a pale emerald green, and is not matched by the blue green which is usually associated with verdigris.

What is usually sold now by the artists' colourmen as verdigris is normal acetate of copper, the true verdigris made by the action of fermenting grape-skins on copper sheets being a sub-acetate. This

sub-acetate is partially decomposed by water, leaving behind a still more basic salt. This basic salt, obtained by boiling true verdigris with a little water, very closely matches the verdigris on the fifteenth century manuscripts.

The explanation, therefore, is probably that the use of verdigris direct on the manuscripts was found objectionable owing to its being partly soluble in water, which would spread through the parchment and round the place where the paint was laid on, and, therefore, in order to prepare it for use on the manuscripts, it was probably treated with water to a limited extent, thus producing a product closely resembling the basic salts left on boiling with water, and it was this verdigris from which the greater part of the soluble matter had been removed that was used for painting purposes.

I have not investigated the matter further, as having succeeded in producing a product so closely resembling fifteenth century verdigris, it was not necessary to make further experiments, but I should like to note in passing that the residue left on boiling contains two different crystalline substances, pointing to the probability that these basic acetates of copper would be worth a fresh investigation, with a careful study of their crystalline properties with a view to finding out how far the supposed basic salts may consist of mixtures.

The only other greens of copper origin which are doubly refracting, are malachite in some cases, and emerald green. The distinction between emerald green and verdigris is usually to be decided by matching under a microscope and can further be

confirmed by the application of tests for arsenic which will be discussed under the head of Scheeles' green.

Transparent Copper Green.—In the course of the examination of illuminated manuscripts from the eighth to the fifteenth century, I repeatedly found a bright grass green used which, under the microscope, appeared to be quite transparent, and free from crystalline particles. I was fortunate enough to be able, in a certain case, to obtain one or two tiny microscopic samples of this green. The ferrocyanide test revealed that it was a copper green, and not a vegetable green as I had at first imagined, and examination between crossed nicols confirmed the conclusion come to by examining the separated particles under the microscope that it had no crystalline structure at all, consisting of a uniform transparent layer. The particles were treated with water, alcohol, and chloroform, and did not show any signs of dissolving in any of them. On searching carefully through mediæval manuscripts, no receipts were found for the preparation of a green which could in any way account for this substance, the earliest receipt which seemed applicable being the one given by De Mayerne (Sloan's MS. 2052) taken from the receipts of Bouffault (Par. 62, "For making a green by dissolving Verdigris in Venice Turpentine"). Modern chemists are, of course, familiar with copper resinates of this character. I have found that it is quite easy to dissolve copper acetate in Venice turpentine, common rosin, or Canada balsam so as to make a beautiful transparent green, which exactly corresponds in appearance under the microscope with this green which is found on

the illuminated manuscripts. If I used Canada balsam, the particles of the green resisted the action of solvents, but if prepared from Venice turpentine, they at once dissolved in alcohol. I have also experimented on balsam obtained from the cedar, which I found is insoluble under these conditions just like Canada balsam. The insolubility, therefore, of these ancient fragments, if we assume them to have been made in this way, is to be accounted for either because of age, the copper resinates being in themselves very insoluble, or because in the case of the particular sample I happened to examine, the balsam used for dissolving the verdigris was not a pine balsam, but one obtained from another source, such, for instance, as the cedar.

Various tints of green can be obtained by introducing a little saffron along with the copper acetate, which will be perfectly permanent under these conditions. While, therefore, it cannot be absolutely proved up to the present that the green on the illuminated manuscripts is prepared in this way, I know of no other method of obtaining a transparent copper green free from crystalline structure, and certainly my preparations matched remarkably well the appearance under the microscope of those upon illuminated manuscripts.

The further question arises as to how this green was applied. This can be done in more than one way. It could be painted on hot, which is an unlikely method, as the manipulation is troublesome, or it might be diluted with a little spirits of turpentine. As will be explained later, when discussing the history of

artists' mediums, the earliest literary evidence of the use of turpentine by artists is in the sixteenth century manuscripts, while the earliest actual evidence that I have been able to find is on a late fifteenth century manuscript. At the same time, the art of distillation was known from Classical times, to the alchemists, and it is not inconceivable that the dilution of green formed by dissolving copper acetate in balsams was obtained by adding oil of turpentine. It can, however, be used in two other ways. If the green, on being formed, is spread out in thin layers, and is then kept at the temperature of boiling water for some days, it can be scraped off and ground into a powder, and this powder can then be mixed with gum or white of egg, and when dry it is very difficult to distinguish from the painting done with the green product direct. Moreover, the presence of white of egg, if used, might be another reason for the particles obtained for the microscope being so insoluble, as the white of egg would protect from the action of solvents such as alcohol.

Another method which will be discussed later is to emulsify it with egg.

Another very curious fact was that on one of the particles examined, some crystals were noticed which were partially dissolved in the mass of the green. These crystals on examination proved to be azurite, and not copper acetate as was expected. It therefore looks as if, in the case of this particular sample, the azurite had been the original source of the copper. Azurite could not be used directly, as it does not readily dissolve, and if the temperature is raised, it

ultimately decomposes. As the azurite does not dissolve except to a slight extent it must have been converted into a soluble salt, and therefore the only way in which I can conceive of this green having been prepared is, that first of all azurite had been treated with vinegar, evaporated to dryness, and the residue then dissolved in pine balsam. We must suppose that one or two crystals of azurite had escaped decomposition.

The nature of the copper green has been further confirmed by the following experiments.

Particles were treated with the tin bromide preparation described on p. 156, and also with strong sulphuric acid, and, at the same time, copper green of my own preparation painted on direct and another portion which had been dried and ground and mixed with gum were treated.

In all these cases the tin bromide reaction produced a brown violet discoloration, thus indicating the presence of a resin, but on treatment with sulphuric acid, the copper green from the MS., and the copper green mixed with gum, resisted the action of the acid for a long time, while the pure copper green was at once attacked. These results therefore seem to indicate that the green has been prepared by dissolving in a balsam and then painted on either by emulsifying with egg, or drying, grinding and mixing with egg or gum.

Later on, I shall discuss the question as to whether a green of this kind was not used by the early "oil" painters, as it seems to be the only way of accounting for the magnificent green seen in the pictures of Van Eyck and his immediate followers. I had been driven to this conclusion before suspecting its exist-

ence on illuminated manuscripts. It certainly shakes one's confidence in the receipts for pigments to be found in mediæval manuscripts when a green which was used from the ninth to the fourteenth century throughout Europe and in Byzantium is not described in any of them.

This green can be identified by its appearance under the microscope, as already described, and by the help of the ferrocyanide test.

Egyptian Blue.—The result of the examination of Egyptian blue by Russell, Fouqué and myself, is to establish finally that it is a definite crystalline silicate which agrees roughly with the formula, $CaO,CuO,4SiO_2$, although these metals can be partially replaced.

It has the following optical properties :—

It is doubly refracting, and in convergent polarised light displays the cross and ring characteristic of uniaxial minerals, thus distinguishing it sharply from azurite. The crystals offer remarkable pleochroism, changing from deep blue to pale rose.

It is insoluble even in boiling hydrochloric acid, but if a portion is treated with acid potassium ferrocyanide, very often here and there small quantities of the red copper compound are formed, owing, no doubt, to incompletely combined copper. If painted out and then examined under the microscope it might well be mistaken for badly washed ultramarine, owing to the presence of large quantities of uncombined quartz mixed with the blue crystals, but if a portion is removed for examination, it is of course impossible to mistake the one mineral for the other, owing to the characteristic properties both of Egyptian blue itself and of the quartz fragments with which it is mixed.

After a little experience, the direct examination on the painted surface is reliable, as the tint of the ultramarine particles is quite different to the Egyptian blue crystals.

Ultramarine Real.—Real ultramarine is prepared from lapis lazuli and is a compound of silica, alumina, soda and sulphur, and is now prepared artificially by heating these materials together. Lapis lazuli itself, however, contains several other minerals besides ultramarine such as Haüynite, Sodalite, and frequently iron pyrites, to which the little gold sparks in the stone are due. When therefore the lapis lazuli is ground to powder, it appears of a bluish-gray colour, and on examining under the microscope, the deep blue particles of ultramarine are seen mixed with a large quantity of colourless minerals. The ultramarine itself gives no reaction between crossed nicols, but some of the colourless minerals with which it is associated are doubly refracting, so that its appearance under the microscope with ordinary light, and also between crossed nicols, is very characteristic. On moistening with a weak acid it is at once bleached, thus behaving in the same way as the modern artificial ultramarine, but is easily distinguished from it, as artificial ultramarine consists entirely of blue without any intermixture of colourless minerals, and gives of course no reaction between crossed nicols. The direct identification of ultramarine under the microscope is usually quite easy, as the deep translucent blue is readily recognised, while a certain amount of the other colourless minerals is always present. The

success with which the separation of the ultramarine from the lapis lazuli has been carried out can be roughly determined by the proportion of the particles of blue and of the colourless minerals present.

The mediæval method of preparing the blue was to make up the lapis lazuli into a paste after grinding finely, sometimes assisting by heating first, with a mixture of resin, beeswax, and linseed oil. This mass was then kneaded under water slightly warm, and sometimes containing a little potassium carbonate. In this way the blue was extracted with more or less of the colourless minerals. This is, I believe, still the best way of separating ultramarine, as it is difficult to make a successful separation by ordinary grinding and floating, while the more complex methods of the mineralogist with heavy solutions are not suitable for commercial purposes. I have prepared ultramarine in this way from lapis lazuli quite successfully, and it will be found when we come to deal with the history of ultramarine that its successful separation from lapis lazuli was very slowly arrived at, the early ultramarine containing large quantities of the colourless minerals. It is only after the twelfth century that at all a perfect separation is obtained.

The main source of ultramarine is at Badakshan on the Kokcha, a branch of the Oxus, for which the natural trading centre is Bokhara. This seems to have been the main source from which it has been obtained for a very long time, as these mines were visited and described by Marco Polo. It occurs in other places in Asia and South America.

Azurite.—Azurite or Chessylite, the basic copper carbonate, is a native copper mineral belonging to the monoclinic system. It is found in beautiful crystalline masses, but also massive and dull and earthy. The existence of different varieties have no doubt led to its appearance in the history of painting under different names, but in so far as I have been able to trace it on actual illuminated manuscripts and pictures, it has always been of a fine crystalline variety. It is easily identified in the first place by its appearance under the microscope, consisting of transparent blue and greenish crystals with little or no admixture of colourless matter. The crystals are usually slightly green, and it effervesces with acids, gives the copper reaction with acid potassium ferrocyanide, is doubly refracting between crossed nicols, and gives with convergent polarised light the figures characteristic of a biaxial, positive mineral, while its refractive index is about 1·9.

These reactions between crossed nicols distinguish it from Egyptian blue on the one hand, and from the artificial copper carbonates or blue verditer on the other, as they do not give any reactions with polarised light. It is found in many places in Europe, such as Chessy near Lyons, and Redruth in Cornwall, while it is evident from the statements made by Pacheco that it was obtained early in the sixteenth century from some source in Hungary. It also occurs in Germany, and in modern times magnificent deposits have been found in America. It is curious that it is referred to by De Mayerne as coming from India.

Ultramarine Ash.—Ultramarine ash is quite easily recognised under the microscope, as it consists princi-

pally of the colourless minerals contained in lapis lazuli with a little of the ultramarine scattered through, and therefore obeys all the optical and chemical tests which apply to ultramarine.

Blue Verditer.—Receipts for making what are called azures are very old, and are to be found in the manuscripts of Jehan Le Begue and in those of later date. Some of these receipts are practicable working receipts others are quite impossible.

Among them is to be found the treatment of a copper salt with lime or potash and the introduction of a certain amount of sal-ammoniac. This seems to be the recognised way of making blue verditer to-day, the receipt given by Hurst in "Painters' Oils and Colours" consisting of the precipitation of copper sulphate by lime and carbonate of potash, and then treating for some days with ammonium chloride and sulphate of copper.

Analysis shows blue verditer to consist of a basic carbonate of copper which sometimes contains calcium sulphate and sometimes a little copper sulphate. The manufacture of blue verditer seems to have been carried on in England in large quantities at one time, and the pigment can still be obtained from the artists' colourmen.

It is readily recognised by the fact that like azurite it gives the deep red precipitate under the microscope with an acid solution of potassium ferrocyanide, and it effervesces with weak acids. It can be distinguished from azurite by the fact that it is not doubly refracting, and that when immersed in oil of Cassia, its refractive index is below oil of Cassia instead of above.

Green Verditer, like Blue verditer, is a basic carbonate of copper, the difference in tint simply depending upon the conditions under which it is prepared. It can be recognised by giving the red coloration with acid ferrocyanide and effervescing with acids, and can be distinguished from malachite with certainty by immersing in oil of Cassia, its refractive index being below, while malachite is above that of oil of Cassia. As a rule, some particles of malachite are doubly refracting, but this double refracting test cannot be entirely relied upon.

LAKES.—Kermes is the product of a small insect resembling the cochineal insect which grows upon the prickly oak round the shores of the Mediterranean, and a dye can be obtained from it very similar to cochineal, while it forms lakes which agree closely with the cochineal lakes in their appearance and properties, although not quite so brilliant in colour. On exposure to light it has about the same permanency as cochineal.

Sapan Wood is a dye wood which is obtained from Ceylon, and which corresponds closely to the Brazil wood which comes from Brazil. A violet colouring matter can be extracted from it, which forms fugitive crimson lakes.

Lac Lakes.—The colouring matter for lac lake is obtained from resin which is due to the *Coccus lacca* which lives on the twigs of trees of the species Butea, Ficus and Croton. These insects become embedded in the resin which exudes from the tree, forming a red resinous mass which is known as stick lac, and from which the dye can be extracted, leaving the resin known as Indian lac. If the resin is boiled in water

containing a little alkali, and the solution evaporated with the introduction of a little alum, the dye is obtained in a condition ready for transportation. Fine crimson lakes can be prepared from this dye.

The *Cochineal* insect (*Coccus cacti*) is obtained from Mexico, and a fine crimson dye can be extracted by boiling in water with alum or an alkaline solution, from which crimson lakes are obtained. The crimson lakes of the modern artist's palette are prepared from this dye.

Madder.—The dyes obtained from the madder root by a process of fermentation, the dye consisting principally of alizarin and certain other allied compounds. Alizarin is in itself a deep orange-yellow substance which can be dissolved with alkaline solutions forming a deep purple solution.

All these lakes are prepared by a similar process, that is to say, the dye is either dissolved in alum or in a solution of carbonate of soda, and then by mixing the alum and the soda together, a precipitate of hydrate of alumina is thrown down which is dyed with the lake. The brilliancy of the resulting colour depends upon minute details of the conditions under which the precipitation took place, and which we need not consider here.

On exposure to light, the sapan wood lakes are the most fugitive, the lake kermes and cochineal lakes are of about the same permanency, while by far the most permanent of all are the lakes prepared from the madder root.

Lakes from cochineal or from kermes seem to be quite sufficiently permanent for use on illuminated

manuscripts where they are seldom exposed to light for any length of time, but they prove fugitive when used for painting purposes, unless specially protected. If, however, they are locked up in a pure resinous medium, such as Venice turpentine, they prove to be quite permanent when exposed to light.

It is a very difficult matter to distinguish microscopic particles of these lakes one from the other, but by means of the following tests it is possible to distinguish madder lake in some mediums from the others.

If small particles of the lakes are exposed to the action of moist sulphur dioxide gas, madder and brazilwood lakes are quickly bleached, kermes bleaching more slowly to a faint purplish tone, while both cochineal and lac lakes resist the action of sulphur dioxide for a very long time.

On treating the lakes with ammonia, they are all rendered very purple in tone, but in the case of the cochineal lakes, a very deep violet solution is formed surrounding the particle of lake. If brazilwood lake is treated with quite a weak acid, like acetic acid, it is at once bleached yellow, while the other lakes are little affected.

The best reaction to distinguish madder lake from the others, is to cover the particle of lake on the slide with a thin film of collodion and then treat with dilute nitric acid. All the lakes are apparently bleached, but if the slide is then immersed in ammonia, the madder lake at once turns purple, while the other lakes remain unaffected. Care has to be taken that the action of the nitric acid does not go on too long, in which case the madder lake will also be oxidised and

destroyed, and will not, therefore, give the purple with ammonia. In applying this test it is as well to have some particles of the lakes themselves on the slide along with the sample to be examined, as a check for comparison during the reaction.

Tyrian Purple.—This beautiful pigment is derived from the *Purpura haemastoma*, and from *Murex brandaris*. The colour-producing secretion is contained in a small whitish cist, or vein, and if the pus-like matter, either diluted with water or undiluted, is applied to bits of white linen and exposed to sunlight, it rapidly changes, the colour passing from yellow to green, then to blue, and finally the purplish red or crimson. To produce this change of colour, the light of the sun is essential.

The resulting dye is insoluble in water, alcohol or ether, and sparingly soluble in boiling benzene or glacial acetic acid, but is readily soluble in boiling aniline. Its constitution has been investigated by Friedländer (Ber. 1909, 42, 765), who prepared it from *Murex brandaris*, and found that it was a dibromindigotin. Probably, in order to prepare lakes, the secretion would be stirred up with a suitable paste and exposed to the sun.

These are the principal pigments found on illuminated MSS. up to the close of the seventeenth century. I shall next proceed to deal with other pigments ancient and modern, which it is sometimes necessary to identify.

Smalt.—Smalt is essentially a glass coloured by cobalt, and is prepared by mixing roasted cobalt ore in a furnace, with silica and potash, so as to form a

cobalt potash glass. The tint is violet blue, and, when examined under the microscope, the particles can at once be seen to consist of broken fragments of glass, while if immersed in oil of Cassia, it has a very low refractive index. If examined through the micro-spectroscope, two absorption bands are clearly seen in the red and in the yellow, while a certain amount of red is transmitted, as well as blue and green. These absorption bands can even be seen if the light from a small electric arc is thrown upon a surface painted with smalt, and the reflected light from the surface examined through the spectroscope. Even when mixed with white lead and the surface of the picture examined through the microscope, the smalt can usually be at once identified by its violet blue shade, and by the curious square-shaped points standing out from the white lead, these sharp corners being peculiar to the crushed glass, and not found in the case of other blue pigments, while the powder itself is comparatively coarse when compared with precipitated blues.

A section in oil is not decomposed by acetic acid, but if the section is warmed with strong hydrochloric acid, the smalt is at once decomposed.

Prussian blue is prepared by oxidising the precipitate formed when sulphate of iron is mixed with potassium ferrocyanide. Being a precipitated pigment, the particles are very small, being only slightly granular at 200 diams., and thus distinguishing it from all the other blues with the exception of indigo. The most characteristic reaction for identifying it is to moisten the section with caustic

potash, when the Prussian blue is at once destroyed, the colour being restored by treating the section with dilute acid.

Cobalt blue, like smalt, owes its colour to the presence of cobalt, but is a compound of the oxides of cobalt and alumina. When a section in oil is examined, the particles of cobalt blue will be noticed to be fairly coarse, approaching azurite and real ultramarine in coarseness, but they have no crystalline character. Cobalt blue is very insoluble, and with difficulty attacked. If, therefore, the section is warmed with strong hydrochloric acid, the cobalt blue is left unaffected. When examined through the microspectroscope, it shows the absorption bands in the red and yellow, and the bright red band characteristic of smalt. The simplest method of confirming its presence is the borax bead, as a very minute quantity is sufficient for this reaction.

Artificial ultramarine is prepared by heating together kaolin, sodium carbonate, coal, and sulphur, and is chemically the same compound as is extracted from lapis lazuli. Its appearance under the microscope is, however, quite different, as all the particles are blue, and are finer than those obtained by the preparation of ultramarine from lapis lazuli, lying in size between Prussian blue and cobalt blue. When examined between crossed nicols it shows none of the characteristics of lapis lazuli, owing to the absence of the colourless doubly refracting minerals which lapis lazuli contains. Its most characteristic reaction is its easy destruction by a dilute acid. If, for instance, a section contains white lead and ultramarine, the dilute acetic

acid, while dissolving the white lead, at once destroys the ultramarine. In the case of lapis lazuli, a residue of doubly refracting crystals is left, while in the case of the copper blues, which are more slowly destroyed by the weak acid, they are easily recognised by the potassium ferrocyanide test.

The presence of ultramarine can be further confirmed by coating the particle with collodion, and then wetting with a mixture of acetic acid and lead acetate. The particle turns black.

Naples yellow is supposed to have been originally a native yellow found on Mount Vesuvius, but for centuries has been a compound of lead and antimony oxides, and is now prepared by fusing together tartar emetic, lead nitrate and common salt. It is still used in pottery manufacture, but what is sold as Naples yellow by the artists' colourmen is a mixed yellow which imitates the tint. The oil film is turned a dirty brown by sodium sulphide, is not attacked by acetic or hydrochloric acid, but dissolves in nitric acid.

Lead Chrome.—The lead chromes are compounds of lead and chromic acid, the lead chromate being prepared of several tints, the normal chromate being a bright yellow, while the basic chrome is a deep orange red. They are seldom pure compounds of lead chromate containing lead sulphate, and often other substances such as calcium sulphate and calcium carbonate. If treated with sodium sulphide in the oil film they are blackened, and are also slowly blackened by an acid solution of sulphuretted hydrogen. If a surface painted with lead chrome is moistened with caustic soda, two tiny platinum electrodes pressed

upon it connected with about four volts, a green reduction is obtained underneath the negative electrode. They are practically unattacked by acetic acid, converted into a white mass by hydrochloric acid, and little affected by nitric acid. If left in contact for some time with a solution of silver nitrate and acetic acid, they are gradually converted into the red silver chromate, and if a little mercury is partially dissolved in nitric acid and a drop placed on the particle of chrome and evaporated to dryness, a deep orange coloration is obtained.

In addition to lead chromates, *barium chromate* and *strontium chromate* are used in painting. They are both dissolved from the oil film by hydrochloric acid, and give the same reactions as lead chromate with silver and mercury salts.

Cadmium yellows are compounds of cadmium and sulphur, and vary in hue from pale lemon yellow to orange. The oil film is attacked and dissolved by hydrochloric and nitric acid. It is unchanged by sodium sulphide, and at once turns black if covered with a solution of silver nitrate containing a little acetic acid.

Cobalt yellow is the double nitrite of cobalt and potassium. The oil film is not attacked by acetic, hydrochloric or nitric acids, turns black with sodium sulphide, and dark brown with caustic soda.

Scheele's green.—This green is an arsenite of copper, it is much more brilliant than the copper carbonate greens, and can therefore be approximately identified by matching under the microscope, and differs from emerald green in being non-crystalline and not

doubly refracting, while it dissolves in acids without effervescence.

The most useful test for identifying it as a compound of arsenic in the oil film is stannous chloride test.

For this purpose place on the slide a sample of verditer and Scheele's green in oil beside the unknown sample, coat the whole with collodion and immerse in a bath of stannous chloride dissolved in strong hydrochloric acid.

Then very gently warm to about 60°. The verditer dissolves, but the arsenic green becomes brownish-black. For the additional test with Thorpe's apparatus see emerald green. *Chrome greens* are a mixture of Prussian blue with chrome yellow. If the oil film is treated with caustic soda, the Prussian blue is destroyed, leaving the yellow pigment behind.

Emerald green is a copper aceto-arsenite, consisting of green crystals which are doubly refracting, and with a refractive index above oil of Cassia. If treated with acid potassium ferrocyanide they give the brown coloration of a copper green, and with stannous chloride and hydrochloric acid give the brown reaction for arsenic.

The arsenic greens can be in addition tested for in Professor Thorpe's modification of Marsh's apparatus, the only difficulty being to ensure that the green is dissolved from the oil and that no arsenic is introduced during the process. A very good method is to start the Thorpe apparatus with purified sulphuric acid and allow it to run for a short time so as to ensure that the sulphuric acid is free from arsenic, then remove a little of the acid from the apparatus, concentrate, and use

the concentrated acid to dissolve the pigment with heat, dilute and return to the apparatus.

Viridian or Green Oxide of Chromium.—This green is a chromium hydrate; it appears transparent when examined under the microscope. The oil film is not attacked by acetic, hydrochloric, or nitric acids or caustic soda.

In conclusion the following tables contain a summary of the reactions which have been described as determining these various pigments even when embedded in dried linseed oil, with the exception of the lakes. As has already been explained, these reactions have been selected from a large number, as those which are visible under the microscope and which can be relied upon to take place in presence of the dried oil film, and which do not involve the solution and then the testing of the dissolved particle of paint, so that very minute fragments are quite sufficient for the purpose. In these tables the pigments are supposed to be pure. The most common pigment for them to be mixed with is white lead which can be removed by repeated treatment with dilute acetic acid. In cases where the pigment itself is also soluble in acetic acid, some test must be used to identify it which does not involve the removal of the white lead, though in some cases, by carefully watching the particle while treated with the acid, on account of the white lead being so rapidly attacked, it is quite possible to isolate a few particles of the pigment. It will also be noticed that a very large number of the reactions selected are independent of the question as to whether white lead is present or not.

TESTS FOR RECOGNISING MICROSCOPIC FRAGMENTS OF CERTAIN PIGMENTS IN A DRIED OIL FILM

These tables are merely a summary and must be read along with the description of the pigment in the text.

YELLOWS.

	Acetic Acid.	*Hydrochloric Acid.*	*Nitric Acid.*	*Sodium Sulphide.*	*Caustic Potash.*	*Silver Nitrate and Acetic Acid.*	*Mercury dissolved in Nitric Acid.*
Lead Chrome ...	Unchanged.	Turns white.	Partly attacked.	Black.	Dissolved.	Red slowly.	Red on evaporating.
Barium Chrome ...	Unchanged.	Turns white.	Dissolves.	Unchanged.		Red slowly.	Red on evaporating.
Orpiment	Unchanged.	Unchanged.	Unchanged.	Dissolved.	Dissolved.		
Cadmium Sulphide	Unchanged.	Turns white with effervescence.	Dissolves with effervescence.	Unchanged.		Black.	
Yellow Lake ...	Dissolves.	Dissolves.	Dissolves.	Unchanged.	Orange.		
Gamboge	Dissolves.	Dissolves.	Dissolves.	Unchanged.	Orange.		
Naples Yellow ...	Unchanged.	Unchanged.	Dissolves.	Brown.			
Lead Oxide ...	Dissolves.	Dissolves.	Dissolves.	Black.			
Cobalt Yellow ...	Unchanged.	Unchanged.	Unchanged.	Black.	Brown.		

ORANGE.

	Nitric Acid.	*Sodium Sulphide.*					
Red Lead	Dirty brown.	Black.					
Orange Chrome ...	Bright yellow.	Black.					
Orange Cadmium ...	Dissolves.	No change.					

GREENS.

	Acid Potassium Ferrocyanide.	*Hydrochloric Acid and Stannous Chloride.*	*Optical Properties.*	*Acetic Acid.*
Verdigris	Deep red.		Doubly refracting, R.I. below Cassia oil.	
Malachite	Deep red.		Doubly refracting, R.I. above Cassia oil.	Effervesces.
Green Verditer	Deep red.		Not doubly refracting, R.I. below Cassia oil.	Effervesces.
Scheele's Green	Deep red.	Black.	Not doubly refracting.	
Emerald Green	Deep red.	Black.	Doubly refracting.	

Notes:—*Cobalt Green* dissolves in HA and gives the cobalt bead.
Viridian is insoluble in and unchanged by HA, HNO_3, and NaOH.
Chrome Green turns yellow when treated with NaOH.

BLUES.

	Acetic Acid.	*Acid Potassium Ferrocyanide.*	*Strong Hydrochloric Acid.*	*Caustic Soda.*	*Chlorine.*	*Optical Properties.*
Ultramarine, Real ...	Bleached.					Colourless, doubly refracting crystals.
Ultramarine, Artificial	Bleached.					
Azurite	Dissolved.	Deep red-brown.				Doubly refracting, R.I. above Cassia oil.
Blue Verditer	Dissolved.	Deep red-brown.				Not doubly refracting, R.I. below Cassia oil.
Prussian Blue	Unchanged.			Bleached.		
Indigo	Unchanged.				Bleached.	
Smalt	Unchanged.		Dissolved.			
Cobalt Blue	Unchanged.		Unchanged.			

Notes:—Prussian Blue and Indigo hardly resolved by 150 diameters magnification.
To confirm Ultramarine, cover particle with collodion, moisten with acetic acid plus lead acetate. The particle turns black.
Confirm Cobalt Blues and Greens with Borax bead. The appearance of Smalt under the microscope is quite distinctive.

To the chemist some of these reactions will be perfectly obvious, while others will appear somewhat unusual. As already explained, the aim has been to obtain either a change of colour in the particle of pigment itself or its solution or refusal to dissolve. In addition many reactions have been rejected because they could not be relied upon in the presence of the oil film. The selection of sodium sulphide instead of ammonium sulphide as a reagent is perfectly obvious from this point of view.

The silver nitrate test for distinguishing cadmium sulphide and the use of silver nitrate and a mixture of mercurous and mercuric nitrate for chromes are, I think, of some interest.

I used an acid solution of a copper salt first for distinguishing cadmium yellow, but found it not always reliable. A silver salt will, of course, ultimately reduce under such conditions, but the blackening of cadmium sulphide is very rapid and marked. Under the peculiar conditions involved it is not safe to rely on any of the ordinary reactions until carefully tested, and for the same reason I have not been able to obtain much assistance from the methods given in books on microchemical analysis. Every new picture examined may, of course, present a new problem, but the following imaginary case will give a good idea of the method of procedure.

A particle of paint consisting of a mixture of blue with white lead has to be examined. The examination of the surface of the picture itself will, under the microscope, probably give some indication, smalt, azurite and ultramarine being each very characteristic.

A sample having been taken, mounted in paraffin, and cut in sections, the section is examined under the microscope, when an approximate idea of the blue paint will probably be formed from its appearance. The section is then gently warmed with dilute acetic acid and carefully washed.

As the white lead dissolves, if the blue is ultramarine it will disappear completely. When the section is clear, if the blue has disappeared, it is examined between crossed nicols, when the characteristic crystals accompanying real ultramarine are easily identified.

If these are absent it is probably artificial ultramarine. This is confirmed by coating another section with collodion and putting on a drop of lead acetate and acetic acid. In a short time the blue will turn black.

If the blue is azurite or verditer it will dissolve more slowly, and if carefully watched some isolated fragments of blue will be found. If azurite, they will give the characteristic reactions between crossed nicols. If verditer, they will give no such reactions, will ultimately dissolve, and another section will give the reaction with potassium ferrocyanide for a copper blue. If the section clears and the blue remains, if very finely granular, it may be Prussian blue or indigo.

Treatment with caustic potash and then with acid at once confirms Prussian blue. The indigo is unaffected but readily bleached.

If the blue is smalt the glassy fragments will be quite unmistakable, and if now warmed with strong

hydrochloric acid the smalt is decomposed. It may further be confirmed by its characteristic absorption bands under the microspectroscope.

A blue in comparatively coarse particles which survives these reactions and is not decomposed by strong hydrochloric acid is one of the modern cobalt blues.

It also gives the characteristic absorption bands, and is most easily confirmed by a tiny borax bead on a fine platinum wire.

The most unsatisfactory reactions are those for lakes. I had hoped in their case to make use of the microspectroscope, but the tiny, partially faded, semi-opaque fragments failed to give the desired results.

CHAPTER V

THE EXAMINATION OF ILLUMINATED MANUSCRIPTS FROM 700 TO 1500 A.D.

It will be noted that in Chapter II it is stated that there is no reference to the preparation of blue from lapis lazuli in classical times, but that on the other hand the blue universally used is the Egyptian blue. It becomes therefore of interest to know whether this blue survived till later times.

In the account given of blues by Mrs. Merrifield, she evidently is under the impression that two blues were known to Italian artists—the old Egyptian blue and smalt.

In Chapter II will be found a brief account of all that is known about the history of smalt, which being a glass coloured by cobalt, has no relation whatever to the Egyptian blue we are now considering.

A careful examination of Mrs. Merrifield's statement will reveal that she has no evidence of the use of Egyptian blue beyond a receipt in the Brussels MS., which is so obviously a copy of the receipt given by

Vitruvius as to have no value as evidence that this blue was made or known.

It has been stated by more than one writer that they have recognised it on illuminated manuscripts, but such statements must be received with caution.

When an authority like Sir Arthur Church states that he has come across it, the position is very different, and one must conclude that it sometimes occurs on early manuscripts. It is, however, not impossible that this occurrence may be due to the blue having been scraped off old Roman frescoes just as Theophilus tells us to use the classical mosaics as a source for coloured glass. In the manuscripts examined by me I have never once found it.

This is all the more remarkable as in the early manuscripts the blue is not only always ultramarine, but ultramarine very badly prepared.

As has already been stated, if lapis lazuli is ground down, the result is a grey powder, as the mineral contains a preponderance of white minerals such as sodalite. It is therefore necessary either to separate the blue by washing and floating, which does not seem to be very efficient, or by the methods described in the MSS. of Jehan Le Begue and later manuscripts.

These receipts consist of making up the powdered stone into a paste with resin, wax, and oil, and kneading the soft mass under warm water containing a little potash. The author has found no difficulty in preparing a fine ultramarine this way, and believes it is still the method used in the trade for its preparation.

As we shall see subsequently, the first appearance of a really fine ultramarine on the illuminated manu-

scripts is only shortly before the earliest publication of the receipts.

Whatever the method of preparation may have been in the earlier centuries, the result was a dull weak blue which, under the microscope, is seen to be full of the white mineral substances already mentioned.

The best ultramarine contains some of them, and consequently can always at once be distinguished from artificial ultramarine by the presence of colourless crystals, transparent in oil, many of which are found to be doubly refracting when examined by polarised light.

The blue found on the early Byzantine manuscripts of about the seventh century onwards is a badly washed ultramarine. Now the interesting point to note is that this poorly washed ultramarine is not so fine a blue as the Egyptian blue. Moreover, the only large and constant source known of lapis lazuli is in the upper valleys of the Oxus, for which Bokhara is the trading centre. Other sources of lapis lazuli are known and others may have been known in former times, but it is probable that it would have to be brought from long distances and then the blue, of which the yield is small, extracted with difficulty. Remembering then that Egypt was part of the Byzantine Empire until conquered by the Mohammedans in the seventh century, one can only suppose that in the seventh century the manufacture of this blue had already ceased to exist.

It is possible that the earliest manuscripts date *after* the Mohammedan Conquest, and the supply of Egyptian blue was cut off owing to that invasion, while the tendency would be for its manufacture to perish

under Mohammedan rule. I think we may safely say it was in universal use in the second century, but by the seventh century its manufacture, carried on, according to Vitruvius both in Alexandria and in Spain, seems to have disappeared.

The process of manufacture was a delicate and difficult one, and therefore in time of political disturbance might well die out. Nevertheless the complete disappearance of this blue, manufactured from as early as the fourth dynasty, and used so universally throughout the Roman Empire, is of considerable historical interest.

Byzantine Manuscripts.

As already stated, the earliest Byzantine manuscript examined (Add. 5111, ff. 10, 11, Brit. Mus.) is supposed to be of the sixth or seventh century, and consists of two leaves from a Gospel book which are entirely covered with gold leaf paint. The pigments used consist of a green which resembles malachite which is mixed with a little blue; a very fine rich coloured lake which matches a modern madder carmine. This rich coloured lake is probably a preparation from the Tyrian purple, as, in the first place, we know of no receipt for a lake made from kermes or madder at that time which could produce so beautiful a result, and, in fact, we shall not get anything so rich in colour again until the late fifteenth century. In the second place, in tracing this colour through the Byzantine manuscripts, we shall find cases where it passes from a crimson to a purple very nearly matching the Irish purple of which

we shall have to speak later. In fact, there is a regular gradation of tint from the deep purple obtained by staining the vellum found both in the East and the West to the purple pigment used on the Irish manuscripts, and from that to the more crimson purples of the Byzantine work and to the rich crimson on this manuscript. If carefully examined, it will be noted that it has got a certain quality of tint about it which is not the same even as crimson or madder lake. While, therefore, it is impossible to speak with absolute certainty, I think we are fairly safe in assuming that this brilliant pigment is prepared from the murex. It differs from the Irish purple either because the murex yields a slightly different dye to the purpura, or because of the different conditions of preparation. I have not yet had the opportunity of myself preparing any of these Tyrian purple lakes. Until this is done, it is impossible to speak more definitely.

The ultramarine is of the badly washed variety already described. That is to say, under the microscope, the unmistakable deep blue particles of ultramarine can be seen mixed with a large percentage of the colourless minerals which the ultramarine contains. At the same time it is not one of the worst examples —in fact, some worse examples will be found later on.

Before passing on to consider the other Byzantine manuscripts, there are two general features of these manuscripts which are worth noting. One is that the ink fades to a rich warm brown colour, quite different to the colour to which the ink on Western manuscripts fades. There are only two methods of preparing ink given in classical and mediæval

receipts—one, the mixing of gum with lamp-black, which gives an absolutely permanent and unchangeable ink; and the other inks prepared by treating salts of iron with preparations of tannic acid. Such inks fade to a brown tint which is quite familiar on Western manuscripts and other documents, and judging by the appearance of the letters on some of these Western manuscripts, the ink has been a mixture of both kinds, and has consequently faded unevenly. The tint of the Byzantine ink is quite different, and suggests that it may have been a bituminous preparation, possibly a semi-liquid bitumen placed directly on the manuscript without further preparation. This matter of the Byzantine ink is worthy of further enquiry and investigation.

The next point is the preparation of the surface of the vellum. It is notorious that the pigments flake off Byzantine manuscripts much more easily than Western manuscripts. This is at once explained on examining the surface of the vellum. Either the Byzantine method of preparation was different, or some different skin was used, because the surface under the microscope has a smooth polish, while even the finest of Western vellums under the microscope is simply a mass of fibres, with a rough surface, and with indications here and there, where paint has scaled off, of the surface having been further slightly roughened before the pigment was laid upon it. This roughening of the surface is not seen on the Byzantine manuscripts, and it is easy to understand how on this highly polished smooth surface the paint would tend to scale off.

The next manuscript examined was a copy of Gospels in the early tenth century (Arundel 547). We find here again gold paint, badly washed ultramarine, vermilion, orpiment, the same rich lake as seen in No. 1 ; ultramarine ash, and a dull green which may be malachite. Some earth colours have also been used which it is not easy to identify.

The lake, which we shall call provisionally Tyrian purple, is as fine in this manuscript as in No. 1.

In this manuscript we have the complete Byzantine palette which occurs again and again, viz., vermilion, orpiment, malachite, or a dull green, badly washed ultramarine, and Tyrian purple.

The next manuscript (Add. 28815) is also of the tenth century, consisting of the Gospels, Acts and Epistles. Here again we have gold paint, badly washed ultramarine, malachite, the earth colours, vermilion, and the Tyrian purple as before, but in this case the Tyrian purple is much more purple in tint than in the last two manuscripts, and does not differ very much from the purple on an Irish manuscript, lying about half-way between that and the Tyrian purple in the first two examined.

The next manuscript (Add. 19352) is a Psalter from the Studium at Constantinople, 1066. Again the pigments are vermilion, badly washed ultramarine, Tyrian purple—much nearer to the tint of the Irish purple than any of the former manuscripts—a rather dull orange yellow, which I did not succeed in identifying, earth colours, and the first instance that we have yet come across of the use of the transparent copper green. I have already considered the nature of

this green very fully, and therefore merely note it here in passing. The preparation of the ultramarine in this manuscript was inferior to that in the last three.

We now come to an eleventh century manuscript (Add. 36929) which is of interest as it is the only case that I came across, except one to be shortly considered, where in the place of the Tyrian purple a crimson lake has been used, corresponding in tint to the lakes found upon Western manuscripts. A pinkish wash of colour has been laid over the background, probably consisting of the same lake, and upon this the gold paint has been laid. The other pigments are badly washed ultramarine, vermilion, and malachite.

The next manuscript (Add. 11870) is from the eleventh to the twelfth century, and consists of "Lives of Saints," by Simon Metaphrastes. Here again the same gold paint is used, the ultramarine is of better quality; vermilion, the usual Tyrian purple, earth colours, and a dull dark green, which I was not able to identify.

We now come to one of the most interesting of these Eastern manuscripts, viz., Psalter of Queen Melissenda, of Jerusalem (Eg. 1139), the date of which is 1131–44. It is quite evident that two different hands have been at work upon this Psalter, the earlier part being Eastern and the later part Western in treatment. This view, which is based upon the character of the design, is certainly confirmed by an examination of the pigments. From folios 1–12, the Eastern artist has been at work; while from folios 202–211 we can trace the work of the Western artist. In the Eastern portion, we have a fine example of Tyrian purple,

malachite, orpiment, vermilion, and, for the first time on an Eastern manuscript, a really fine ultramarine, though not quite up to the quality of the ultramarines which we shall afterwards find on thirteenth and fourteenth century Western manuscripts. In the later portions by the Western artist, red lead has been used, while the ultramarine is not of so fine a quality, and the Tyrian purple has been replaced by lake. It is therefore of interest to note, as we shall find later, that this is our earliest example of properly washed ultramarine, and that the Western artist who completed the Gospel had not in his possession as fine a sample of ultramarine as the Eastern artist. This is all the more curious as we shall not find another example of properly washed ultramarine among Byzantine manuscripts. We shall have to consider this question again in discussing the origin of the receipt used for the proper preparation of ultramarine.

The next manuscript examined (Harley 1810) is a Gospel of the twelfth century. On this manuscript we have the badly washed ultramarine, the blue on the whole inferior to some that we have seen before on Byzantine manuscripts; malachite, vermilion, orpiment, gold paint, and the Tyrian purple. The pigments are badly flaking off this manuscript, and it is a typical example of the smooth polished surface of the Byzantine vellum.

The next manuscript is a Gospel of 1285 (Burney 20). It is evident that on these later gospels, the technical skill in preparing pigments is not what it was, while the palette is no longer so complete. The

ultramarine on this manuscript is very badly prepared —inferior in fact to any of the earlier ones we have examined. The only other pigments are vermilion, a lake which is matched by lac lake—at this time universally used in the West—and gold paint. The Tyrian purple has disappeared, and as far as I am aware from the manuscripts I have examined, does not appear again.

The next manuscript examined is dated 1326 (Add. 11838). Very badly prepared ultramarine, vermilion, and a poor faded lake are the only pigments. It is interesting to note that this disappearance of the Tyrian purple and of orpiment, and the loss of skill in preparing ultramarine, are after the sack of Constantinople by the Crusaders. It would be necessary of course to examine a larger number before general conclusions can be drawn, but this fact seems to be certain, and suggests that the sack of Constantinople by the Crusaders marks a date after which there is a rapid deterioration in the technical arts.

Before passing on to consider the Irish pigments, certain general conclusions can be drawn from the Byzantine manuscripts that I have examined.

It will be noted from the seventh to the fourteenth century, with the one exception of the Psalter of Queen Melissenda, the palette remains unaltered—in fact, ultimately deteriorating—the secret of making the Tyrian purple is apparently lost, while the skill in the preparation of ultramarine is less in the thirteenth century than in the seventh. This bad preparation of ultramarine raises some rather interesting questions.

I have already dealt with its significance as bearing

upon the disappearance of Egyptian blue, and we are left to try to find an answer to the question, why, when the technical methods of preparing ultramarine showed a steady improvement in the West, resulting in an almost perfect separation of the ultramarine from the other minerals, in the thirteenth century, this improvement was not reflected in the East. It has been suggested that in some ways the badly prepared ultramarine is a more beautiful and artistic pigment than the more perfectly separated blue, and that the Byzantine artist had no wish for a different tint. On the whole, however, I think that the history of pigments will show that the artist in the past was not concerned by these somewhat subtle æsthetic considerations, and was always prepared to use the most brilliant pigment he could obtain. There is, however, another possibility, and that is the one of religious tradition, by which all the work of the Byzantine School is so influenced. It is quite possible that just as they were so conservative in their drawing and design, they may have been equally conservative in their palette, and that while they could have purchased or prepared ultramarine of finer quality, they considered that it was irreligious to depart from the tints with which they were familiar on their earlier gospels. Whatever the explanation may be, it is perhaps necessary to make clear at this point that I am not discussing the æsthetic beauty of a given pigment. For instance, I quite agree with some of the students of these ancient manuscripts that the brilliant Tyrian purple of the Byzantine manuscripts is not in itself a beautiful colour, and is neither so fine as lac lake which is used on the

Western thirteenth century manuscripts, nor the purple prepared in the Irish monasteries, but regarding it simply as a technical product, it shows the highest technical skill, and in the same way there can be no comparison, as a technical product, between the ultramarine of the thirteenth century, in Europe, and the ultramarine on the Byzantine manuscripts.

Irish Manuscripts.

The next manuscripts that we shall consider are those of Irish origin. They show a very interesting resemblance in the pigments used to the Byzantine manuscripts which we have just been describing.

The first of these are the Lindisfarne Gospels (Nero D. IV.) at the British Museum, of the eighth century. It is unnecessary here to enter into any general description of this priceless possession of the British Museum, or to describe its history. For our present purposes, it is one of the earliest records we have got of work done in England, but at the same time is rightly classified as an example of Irish work, as it is the product of the monks at Lindisfarne on Holy Island.

This manuscript is especially difficult to examine under the microscope, as the medium has been used very heavily, so that the surface is shiny, and it is difficult to make out the separate particles of the pigments. In fact, had it not been for the experience gained in examining Irish manuscripts of later date, it would have been a very difficult matter to speak with certainty as to some of the pigments used.

The medium looks like a gum of some kind, but whether it is gum arabic or some native gum such as cherry gum, it is, of course, impossible to say. The pigments are in excellent condition, and are adhering well to the parchment, which appears, under the microscope, as quite rough in texture, as compared with the highly polished Byzantine skins.

In place of the vermilion of the Byzantine manuscripts, we find here red lead. It is quite unmistakable. Not only is it matched by modern samples of red lead, but also here and there it is slightly discoloured, having the metallic black appearance which is due to the attack of sulphuretted hydrogen. It is not possible to say whether this red lead has been obtained by roasting lead oxide, or by roasting white lead. Both methods were known in the time of Pliny. I should be disposed to say, from its orange quality, that it has probably been prepared by roasting white lead. It is also, of course, impossible to say whether it has been prepared in the monastery itself, or has been purchased, having been prepared in some centre of lead smelting. It is very unlikely, if it is prepared from lead oxide, that it is of local manufacture, as the preparation of red lead from lead oxide is a difficult operation, and is more easily carried out on a large than on a small scale. If it is the result of roasting white lead, this could quite well be conducted in a small furnace; and if prepared from white lead, the white lead itself might have been prepared by the monks themselves from metallic lead by exposing sheets of lead to fermenting grape skins. Whatever its history, it shows that certainly lead, and possibly

its compounds, were available as articles of commerce at the time of these manuscripts, and I think it is more probable that the pigment was purchased than that it was locally prepared.

The green on these manuscripts is evidently malachite green, which again must have been purchased from some region where malachite was obtainable as a copper ore. It is certainly curious that while such importations were taking place, vermilion does not seem to have been among them.

The blue corresponds with the blue found on the Byzantine manuscripts, that is to say, it is badly washed ultramarine, and must therefore have been obtained by a similar process from lapis lazuli. This pigment alone therefore reveals considerable commercial interchange with the rest of Europe, as we have already shown that the probability is in favour of the lapis lazuli coming from Asia, and the monks must either have purchased the stone and prepared the pigment, or purchased the pigment itself.

The yellow is orpiment, which cannot, I believe, be of Irish origin. At the same time, the orpiment used in Ireland from this date onwards is of a particular quality. It is not very bright, and has a scaly appearance, almost resembling litharge, and is in some cases fibrous in structure. It is not nearly so bright as the highly crystalline orpiment to be found on Italian manuscripts. Orpiment varies considerably according to the sources from which it is obtained, but the orpiment in Irish manuscripts is so characteristic throughout the centuries, that one must suppose that it was all obtained from one source, though there

is no indication where this source of supply can have been.

The next pigment of importance is the fine purple which is peculiar to Irish and early English manuscripts. This I can only suppose to have been prepared from the *Purpura capillus,* which is found round the Irish and English coasts. The Venerable Bede tells us that the Irish monks had obtained the receipt for preparing this purple from the East. (Page 85, "Illuminated Manuscripts," J. H. Middleton.)

I have already discussed the question of the fine crimson which is found in the Byzantine manuscripts, and suggested that it is probably the Tyrian purple from the Murex. The pigment in the Irish manuscripts is much more of the true purple, and approaches much more closely the appearance of the stained pages of vellum found in Byzantine and early English and Carolingian manuscripts, so that it seems to form a connecting link between the stained page and the Tyrian purple used by the Byzantine monks. In appearance the pigment suggests a concentration of the dye with some convenient medium such as gum, rather than the preparation of lake in the proper sense of the word, as there is no indication in it of the presence of a base such as chalk or alumina.

These form the main pigments on the Lindisfarne Gospels. Some of the pages are tinted with a pink wash on the vellum. This pink wash may of course be a vegetable lake, but judging from the fact that no other examples of lake are found in the manuscript, and that the early lakes when they do occur are usually very badly prepared, I think it is much more probable

that this pink wash is simply the Tyrian purple, laid on in a thin wash, and possibly let down so as to prevent it being too dark in colour.

In addition to these pigments some earth colours are used. For instance, the Lion of St. Mark is painted with a yellow ochre. There are also deep brown marginal lines which suggest sepia from their appearance, although it is impossible to speak finally on this point.

The close similarity between the pigments of the Lindisfarne Gospels and the early Byzantine work will be noted, the only difference being the replacement of vermilion by red lead.

I have not had the opportunity of examining the Book of Kells, and the next Irish manuscripts that I have seen are of considerably later date.

There is a very interesting Irish Psalter (A. Ca. 44, Edinburgh University Library) which is supposed to be not later than the eleventh century, and which for reasons I shall give presently I believe to be of a still earlier date. On this manuscript we find exactly the same pigments as those I have already described, viz., red lead, Irish orpiment, badly washed ultramarine, and the Irish purple. There is, however, now a difference in the green which is used. It is no longer malachite, but is replaced by the transparent green which is a compound of copper, and which has already been described. In this manuscript there occur two or three pages which contain no script, and which are evidently intended to be entirely devoted to adornment. One or two of these have been filled up with designs in the Irish style, and with Irish pigments, and one or

two have been left blank, but there is one of these pages which is very remarkable. The margin has been painted in with a little design in Irish orpiment but the whole of the interior is filled in with a dark almost black olive-green pigment, which I have not been able to identify, upon which there are some white scrolls, and in the centre of which are to be found gold letters which at once mark this page out as not having been the work of an Irish monk. We must either suppose therefore that the whole page originally contained designs by an Irish monk which were then scraped out or painted over, or that merely the margin had been done, and the work had not been completed. This view would agree with the fact that there are one or two blank pages further on.

The interesting point is the peculiar nature of the gold with which the lettering is done. The appearance of the gold under the microscope suggests that it is water-worn gold dust from river washings. It is certainly not gold paint prepared by the grinding up of gold leaf, nor is it gold leaf. The particles are coarse, they stand up from the page, and they have been burnished to a certain extent so as to rub one particle into another. They stand up from the page and are not laid on gesso, but on the vellum direct. I shall refer to this again later when dealing with the English manuscripts, but in the meantime it only remains to say that the latest date at which I find this gold on an English manuscript, is the Canterbury Psalter, Arundel, 155, British Museum, dated 1012–23. I have not found cases of raised gold lettering on gesso until the twelfth century, and this curious use of gold

dust seems to me worthy of further enquiry, as it may have been the precursor of the raised gold letter. The decorative effect is very fine, and superior to the gold leaf on gesso, as a more broken surface is obtained. There can be no doubt that this page has been painted at a later date than the rest of the manuscript, probably by an English monk, and it is for this reason that I suggest that the date of this Psalter is earlier than the opening years of the eleventh century.

The next two Irish manuscripts which I have examined belong to a very much later date, being thirteenth century. One is an Irish Psalter (Add 36928. Brit. Mus.), and the other is known as the Rosslyn Missal (18.5.19, Advocates' Lib., Edinburgh).

To deal first with the Irish Psalter, we find that red lead has been replaced by vermilion. The yellow is Irish orpiment; the green is the transparent copper green; the ultramarine is still badly washed, and the Irish purple appears as before.

The Rosslyn Missal is also painted with vermilion, orpiment, badly washed ultramarine, and the Irish purple.

The result of these examinations is, I think, of considerable interest, as they show that not only was the original palette evidently inspired from some Byzantine source, but that the Irish, like the Byzantine monks, were very conservative in their methods. We shall find, when we come to study contemporary European manuscripts, that there is a steady progress in the preparation of ultramarine from lapis lazuli, yet in the case of the Irish, as in the case of the Byzantine manuscripts, the same methods of preparation seem to

have been followed, resulting in the imperfect separation of the ultramarine from the mineral. They have also remained faithful to their Tyrian purple, which disappears very early from European manuscripts, and is replaced by lakes which the Irish monks never seem to have adopted. In fact, the only two changes compared with the Lindisfarne Gospels are the replacement of red lead by vermilion, and the replacement of malachite green by the transparent copper green. It is unnecessary here to speculate as to the reasons for this conservatism, whether it was a question of religious tradition, or whether it was due to the fact that they were not able to obtain the supplies or to learn the methods which were in use in European monasteries.

I have now described the pigments to be found on Byzantine and on Irish manuscripts, and I have counted among the Irish manuscripts the Lindisfarne Gospels. We should be equally justified in recording these as one of the earliest of the English manuscripts, and, as we shall see, there is no marked distinction to be made in the pigments used on the early English manuscripts, and those to be found in Ireland.

English Manuscripts.

The first manuscript examined was about the same date as the Lindisfarne Gospels, being a Canterbury Psalter of about 700 (Vespasian A. I.) On this manuscript is to be found the transparent copper green already described, but apparently malachite has been used as well in certain portions; the ultramarine is fair to bad, and there is vermilion as well as red lead, thus differing from the Lindisfarne Gospels, and there

is a purplish coloured, very poor lake used upon it. It will be noted therefore that it differs slightly from the Lindisfarne Gospels both in having vermilion and having upon it the transparent copper green which occurs later on the Irish manuscripts and also in the presence of a poorly made lake in place of the Tyrian purple.

With reference to the presence of lake, the receipts given for the lakes in the earlier manuscripts translated by Mrs. Merrifield are not such as would result in the preparation of a lake of any brilliance, the materials from which they are made being either kermes or, at a later date, sapan wood from Ceylon. The sapan wood lakes are very fugitive, while the kermes lakes are of about the same order of permanency as crimson lake from cochineal. I have repeated a good many of these receipts, and in every case the result is a purplish-crimson lake which is poor and dull in colour. The lakes prepared from these receipts agree very well with those found upon the earlier manuscripts.

In this manuscript the gold is laid direct on the vellum with no priming, and is gold leaf.

There are also alternate gold and silver letters, the silver letters having blackened. On some of the Byzantine manuscripts, where silver letters have been used, the surface has a very remarkable appearance. Not only is the silver blackened, but the parchment for a certain distance round the silver letters has also blackened, and if the page is turned over, the blackening seems to have eaten through the other side of the manuscript. It is almost impossible that this blackening beyond the range of the original silver can be due to

the silver itself, and it seems much more probable that it is owing to some medium which has been used to attach the silver letters to the surface. In the case of this particular manuscript, not only does this blackening beyond the margin of the letter occur round the silver letters, it also occurs in the case of some of the gold letters where the gold has come off. The peculiarity about it is that in some places where the gold has come off, there is nothing to be seen underneath except the parchment surface, while in other parts, perhaps of the same letter, the black stain is to be seen on the surface, and penetrating into the parchment on both sides.

This peculiar result shows, I think, that whatever the blackening round the silver letters is due to, it has nothing to do with the silver itself, as we have here a similar result where gold has replaced silver. The matter is worthy of further investigation, but I am disposed to think it may be due to the use of a different medium for attaching the gold, a medium which may have been customary in the case of silver. In the old receipts, the usual medium for attaching the gold is white of egg, but we find, at any rate, as early as Cennino Cennini, receipts for making up what we should now call a gold size—that is to say, a very thick varnish, and though the introduction of lead dryers is not advised by Cennino Cennini, it is a modern custom in preparing gold size, and as we know that even in the time of Pliny, preparations of linseed and oxide of lead were made up for medical purposes, it is, at any rate, quite possible the preparation of gold size on modern lines was very early.

If such a medium was used for attaching the silver letters, and if, as we may suppose, it was used at some later date for repairing these gold letters from which the gold had been removed, one can understand that such a medium would soak into the parchment round the letter, and that, ultimately, owing to the lead dryers, it would blacken. I only throw this out as a suggestion, as the whole appearance of these letters is very puzzling, and is certainly worthy of a special investigation.

The next manuscript examined (I.E. VI.) was a Canterbury Gospel supposed to be of the late eighth century. On the whole this manuscript corresponds more closely with the Irish and Byzantine manuscripts in the pigments used than the one already described. The blue is very poor and dull, and has been laid on with a large quantity of medium, just like the blue in the Lindisfarne Gospels, and is evidently a badly-washed ultramarine, The red lead is badly tarnished; the green is malachite ; the yellow is orpiment, and there are some purple-stained pages corresponding to the purple-stained pages in the Byzantine manuscripts and which are probably stained with dye from the purpura.

This manuscript is also interesting on account of the peculiar nature of the gold which has been used, a peculiarity to which I have already referred in dealing with the Irish manuscripts, describing the page with gold lettering to be found on the Irish Psalter (A. Ca. 44. Edinburgh University Library). On examining under the microscope, the letters are evidently made of a coarse gold powder very much coarser than the

powder to be obtained by grinding gold leaf, and the particles instead of being sharp at the edges as the powder prepared from gold leaf is, are rounded, having very much the appearance of kidney potatoes. After laying on, they have been, to a certain extent, burnished, so that the different layers of gold have been rubbed into each other, but the outlines of their original shape are quite obvious. I have examined under the microscope gold dust obtained from river washings in Scotland, and while a large number of the particles are much larger than those appearing in this manuscript, the finest dust resembles exactly the appearance of these particles. There can, I think, therefore, be little doubt that the gold used in this manuscript was not in the first place hammered gold leaf, and then ground into gold paint, but was the finest portions of river-washed gold, separated, and used as a pigment. Perhaps river washings may very well have come from some of the streams in England.

The result of the use of these coarse gold particles is to give a raised surface which, at first, almost suggests the raised surfaces to be found later on, and which are obtained by laying the gold leaf on the gesso, but the surface of this manuscript is not nearly so smooth, and has a finer decorative effect than the gold on gesso to be found at a later date. A very interesting question therefore arises as to why gold dust was used. The use of gold leaf is found from such early times, that it is difficult to believe that gold leaf could not have been obtained if it had been desired ; at the same time the production of gold leaf means that fairly large portions of gold are available

for hammering into leaf, and it is possible that the monks may have been able to obtain this gold dust from some local streams, and had not the means for making or the skill for hammering gold leaf from the gold, and therefore found it easier to sift out the finest of the dust and use it for painting purposes. It is also, of course, possible that it may have been used on account of its finer decorative effect, and that we see in this use of gold dust the first beginnings of the practice that we find later on of laying gold leaf on gesso. In fact it is possible that the laying of gold leaf on gesso may have been an attempt to imitate the fine effects produced by the use of this river-washed gold.

In this connection it is worth pointing out that in the manuscript of Theophilus is found the description of mortars and pestles for grinding gold into a pigment. These descriptions are very difficult to understand, as it is impossible to grind gold into a pigment in this way on account of the malleability of the metal. It is, of course, quite conceivable that what is intended to be understood is the grinding of gold leaf, although he certainly does not say so. It is also possible that a brittle alloy of gold was prepared in some way, and that was ground into a powder. I have, however, never found any gold paint on a manuscript which differed at all from the gold paint prepared to-day by the grinding of gold leaf, with the exception of these two or three early English manuscripts, of which this MS. is the first, and of which the appearance does not suggest a brittle alloy ground in a mortar, but does suggest the rounded surface obtained in river-washed

gold. This use of river-washed gold is worthy of further enquiry to see whether it occurs also on early European manuscripts.

This manuscript is also remarkable for having in certain places a very delicate mauve pigment which, at the time I examined it, seemed to me to look like a crystalline mineral powdered up, and not like a mixture. I have been unable to find any mineral which would give this result. Beautifully tinted mauve coloured spars are often to be found in Derbyshire, but, on pounding up, they lose all the appearance of having any colour. As will be found later on in the sixteenth century, mauves were obtained by mixtures of white, lake and azurite, and a very beautiful mauve can be prepared by mixing ultramarine ash with a little lake. When mixed with lake, a careful examination shows the particles of lake here and there mixed with the ultramarine ash, but there is another way of preparing mauve which corresponds more closely with certain receipts given by Pliny, and that is to take the ultramarine ash and mix the dye with it, and then evaporate the whole solution with a little alum in order to fix the dye upon the mineral. If this is done, there are no separate particles of lake to be seen, but, at the same time, the particles of blue remain obvious under the microscope which are mixed with the crystalline substance of the ultramarine ash. This mauve is therefore worthy of further examination, as it is only since I have seen this manuscript that I have been able to determine the nature of the mauves of the sixteenth century manuscripts, and also to prepare mauve by this special treatment of ultramarine ash.

King Edgar's Charter to Winchester. Vespasian A. VIII. The next manuscript examined was King Edgar's Charter to Winchester, 966. This manuscript is of great interest for more than one reason. The number of pigments used upon it is not large, the whole of the letters being painted in gold throughout. The gold lettering on the MS. is entirely done with the river-washed gold described as being used on 1. E. VI. The first page has a wash of pink over the whole of it, which is probably a pink lake. On the margin is to be found a transparent copper green, and ultramarine, badly washed. On another page, the whole of the vellum is painted over with a very bright azurite blue. This is the first time that we have met with azurite, and it does not appear again on any manuscript until a very much later date, and I am disposed to think that it was not an original part of the decoration of the page. Careful examination under the microscope shows that in places where the gold lettering has come off, the blue is lying on the parchment, while in other places, where the gold letters have come off, the clean parchment is to be seen. It is evident, then, that the blue has not been laid on first and the gold lettering on top of it, and yet, on the other hand, the fact that the blue is occasionally covering places which were originally covered with gold, shows, I think pretty conclusively that it was added as a decoration after the manuscript was already prepared, and was old enough for the gold to have come off in certain places. I think, therefore, we are justified in regarding this appearance of azurite as being an addition at a later date, and therefore of no value as

marking the introduction of azurite in place of ultramarine in the tenth century.

Athelstane Psalter, Galba A. XVIII.—The next manuscript examined was King Athelstane's Psalter of the early tenth century. The Calendar at the beginning is painted with red lead, orpiment, badly washed ultramarine, vermilion, and malachite green. Gold leaf paint has been laid direct on the vellum. It will be noted therefore that in this case the river-washed gold dust has not been used.

A fifteenth century miniature has been inserted in the front of this manuscript, and is worthy of examination as showing a completely different palette. The blue is azurite, the green verdigris, ultramarine ash has been used for the delicate greys, and the only pigment common to the early manuscript, is the use of orpiment for a yellow. Gold paint has been used as a pigment, as is commonly found in fifteenth century work, instead of in purely decorative forms.

Canterbury Psalter, Arundel 155.—The next manuscript examined is a Canterbury Psalter between 1012–23. The transparent copper green has been used here as a pigment, and both vermilion and red lead which is badly discoloured, while the ultramarine is now better than in the earlier manuscripts, although still far from perfect.

On the big initial letter two lakes have been used—a red and a purple, both rather dull, the purple resembling pretty closely a lake prepared from kermes. These lakes are just the kind of lakes which one could imagine being prepared in the monastery from the mediaeval receipts, the red lake having been obtained

probably as the result of the introduction of a certain amount of an organic acid like tartaric acid.

The gold used in this manuscript is again the river washed gold dust which was found on I. E. VI.

Winchester Psalter, Arundel 60, (1060).—The next manuscript examined is the Winchester Psalter of the date 1060, corresponding very closely in its pigments with the one last described. Both ultramarine and ultramarine ash, however, have been used here for decorative purposes, the ultramarine is still getting better, but the deep effect seems to have been due partly to burnishing, because where the surface is broken, the ultramarine seems to be badly washed.

The other pigments are red lead, vermilion, the transparent copper green, and a dull purple lake.

Winchester Psalter, Nero, C. IV.—The next manuscript examined is a Winchester Psalter of about 1160. The main change to be noticed in the pigments as compared with the manuscript last examined is the improvement in the ultramarine which is now fairly good, and has been used in large quantities, but has apparently been scraped off in many places at a later time, no doubt to be used upon some later manuscript.

The other pigments are vermilion, red lead, transparent copper green, and a dull purplish lake. There are also some dull greens upon this manuscript which I was not able to identify.

There is a new decorative effect produced upon this manuscript which I have not seen before, by laying gold paint on a yellow ochre underpainting. This, as we shall find, was very common in English work of the

sixteenth century, but as far as I am aware, it is not very often found at these early dates.

Rochester MS. Serm. de temp. (*Advocates' Lib. Edinburgh*, 18, 2, 4).—The next manuscript to be considered is the Rochester Manuscript of the late twelfth century in the Advocates' Library, Edinburgh. This manuscript contains the accounts of a dispute between William the Conqueror and the Bishop of Rochester, and is doubtless of English origin. It contains an initial letter which is of interest, because the pigments used do not correspond at all closely with the pigments which are being used in the Southern English monasteries at this time. Vermilion and the transparent copper green occur, to which we are already accustomed, and the yellow seems to be orpiment, but the ultramarine is badly washed, and corresponds much more closely with the ultramarine on Irish manuscripts, while there is a little touch of the Irish purple. This certainly suggests that the monk employed in painting this inital letter was from an Irish monastery, and brought the pigments with him which he was accustomed to use, instead of utilising the pigments which were to be obtained in the South of England.

Rivaulx Abbey. 6. *C. VIII.*—The next manuscript is one from Rivaulx Abbey of the late twelfth century. The pigments are laid on here very thick and heavy, and the ultramarine is distinctly inferior to that in the manuscripts of this date—with the exception of the preceding one. The other pigments used are vermilion, transparent copper green.

The ultramarine to be found on certain other

Northern and Scottish manuscripts that I have examined, suggests the possibility that in the Northern monasteries, the pigments were not so well prepared as in the Southern monasteries. This may have been due either to the monks not being so successful, or if the ultramarine was purchased instead of being prepared from lapis lazuli, owing to their not being so closely in connection with the best markets for obtaining the pigments for illuminating purposes. I think that we may say that in the matter of the preparation of ultramarine at these early dates, the northern monasteries lay halfway between the work done in the Southern monasteries, and the work done in Ireland.

Westminster Psalter, 2. *A. XXII.*—The next manuscript examined was a Westminster Psalter of the late twelfth century. This manuscript shows certain new departures from those formerly examined. In the first place, we find here, for the first time, burnished gold leaf laid on gesso. The gesso has been laid upon the parchment, and has then been covered with bole upon which the burnished gold leaf is laid. If the receipts for laying gold leaf upon gesso given by Cennino Cennini are examined, it will be found that it was customary to cover the gesso with bole, which is a clayey variety of red ochre, and to lay the gold leaf upon this. The same custom is followed by the gilder of to-day when he is doing what is now called water gilding—that is to say, when he is laying gold leaf with white of egg instead of gold size.

The ultramarine is now fine in quality, and superior to any that we have seen at an earlier date. The other pigments are the same, consisting of vermilion,

a very orange shade of red lead, a dull purplish lake, and transparent copper green. There is also apparently red ochre used on this manuscript which may very well have been the bole used in laying the gold leaf.

English Psalter, 1. *D. X.*—The next manuscript examined is an early thirteenth century English Psalter, certainly written before 1220. The ultramarine is good, but not quite of the finest quality, the other pigments are red lead, vermilion, a pinkish coloured lake, malachite, and transparent copper green, while there are some blackened letters which have apparently been done with silver. The gold is burnished and laid on gesso with red bole.

Petrus Comestor, 3. *D. VI.*—The next manuscript examined is dated 1283. The ultramarine on this manuscript is of the finest quality, while the other pigments are transparent copper green; a fine transparent yellow which is probably orpiment, but it is a little difficult to decide with certainty; red lead, vermilion, ultramarine ash for the grey background, and burnished gold leaf. In addition, the lake on this manuscript is exactly matched by lac lake.

It is very difficult to say from the receipts given in thirteenth and fourteenth century manuscripts whether by lac lake is meant lake prepared from Indian stick lac, or the pigment obtained from Ivy gum which is referred to more than once as exuding as a transparent red pigment. Lac is a product obtained from certain trees in India of the species Butea, Ficus and Croton, by the attack of an insect corresponding to the cochineal insect, the result of the attack being

that the resin from the tree exudes and becomes dyed with the bodies of the insects, the final product being known as stick lac, and being a pink-coloured resin. If this resin is boiled in water containing a little alkali, a great part of the dye is extracted and can be evaporated to dryness and is sold as a dye, while the resin, now deprived of most of its colour, is known as shellac. This dye seems to have been imported into Spain and Provence as early as 1220 so that it is very likely that the dyers would, at the same time, either sell the Indian product as a lake, or prepare a lake from it. Lac lake is still to be found among the lists of artists' colourmen, and it exactly matches the lake which we now find common to European manuscripts during the late thirteenth and fourteenth centuries. The uniformity of the lake is sufficient to show that it is not of domestic manufacture, as it is necessary to make lake in very large quantities and with the highest technical skill to turn out one batch exactly like another, and it is very seldom found at the present day that the lakes from two different manufacturers, although made from the same materials, exactly match. The fine quality and uniformity therefore of these lakes, is, I think, sufficient to prove that they were no longer made in monasteries, but were purchased, and were probably supplied from a common source, while the fact that they match so exactly lac lake, justifies us, I think, in assuming that it is at any-rate highly probable that they were obtained from India.

It is, of course, possible that they are Kermes and not lac lake, and the difference in tint is not very marked, but whether lac or kermes, they must have

been manufactured and distributed from a common centre. I shall refer then in future to this particular tint in lake which is found on the late thirteenth and fourteenth century manuscripts as lac lake, although the evidence is not absolutely conclusive that this is its origin.

Egerton 1151.—The next manuscript examined was a Book of Hours of the thirteenth century in which we again find perfect ultramarine, the other pigments being vermilion, transparent copper green and gold leaf raised and burnished on gesso covered with bole. The lake on this manuscript is somewhat dull and is not quite up to the quality of the one last described. The copper green looks as if it might have been painted over a first painting of malachite. There are one or two other cases where this appearance occurs, but it is difficult to be certain whether a mixed green has been used or not.

Ruskin Bible.—This is an illuminated Bible in the Advocates' Library, Edinburgh, so called because it was formerly in Mr. John Ruskin's possession. It is a very fine example of late thirteenth century work. The ultramarine is of fine quality, the other pigments being vermilion, red lead and lac lake.

Hyrdmanniston Breviary. (Adv. Lib. Edin. 18. 2. 13 *a.*).—This manuscript is supposed to have come from a northern monastery. It is about 1300. The red is vermilion, and the manuscript of interest, because the ultramarine is badly washed, thus agreeing with the case we have already seen where the ultramarine prepared in a northern monastery is not so good as that prepared in the south.

St. Giles Bible. (18.1.2).—The next manuscript is the St. Giles Bible which is supposed to be late thirteenth century work. The gold leaf is on a raised gesso ground, the other pigments being vermilion, green, fairly good ultramarine, red lead, and faded lake. There is also a faded brownish yellow which is probably a lake.

East Anglian Psalter; Arundel 83.—The next manuscript is an East Anglian Psalter of the early fourteenth century. The pigments here are vermilion, red lead, transparent copper green, lac lake, and fine ultramarine.

Luttrell Psalter. East Ang. 1340.—The next manuscript examined was the Luttrell Psalter. This manuscript is of interest for two reasons. In the first place the mauve which has already been described as occurring on Canterbury Gospels (I. E. 6) is again to be seen here. The other pigments are red lead, green, and a lake a little poorer than that on some of the other fourteenth century manuscripts, but apparently the same lac lake occurs. The special interest lies in the blue which is no longer ultramarine, but is azurite. Azurite, we shall now find occurs very often on manuscripts from about the middle of the thirteenth to the middle of the fourteenth century, and I have found it, for instance, on a Flemish Psalter which will be shortly described, of between 1230–50.

The Flemish manuscripts of this period are remarkable, according to Mr. Herbert, for a fine dark blue which is different in quality to ultramarine, and this Flemish manuscript to which I refer was given to me by Mr. Herbert as a typical example of this blue,

and on examination it has proved to be azurite. At the same time it is an azurite differing a good deal in appearance from the very brilliant blue azurite which will afterwards have to be discussed as appearing on late fifteenth and sixteenth century manuscripts, and therefore was probably obtained from a different source. It seems to disappear again about the middle of the fourteenth century, being replaced by ultramarine. This MS. is the earliest date at which I have found azurite on an English manuscript. It will also be noted that the transparent copper green has here been replaced by malachite.

Psalter. Eleanor de Bohun. 18.6.5.—The next manuscript is the Psalter and Hours of Eleanor de Bohun, Duchess of Gloucester, the date of which lies between 1382 and 1399. This manuscript is in the Advocates' Library, Edinburgh. The illumination is in the style of the English monasteries. The ultramarine is of good quality, the lake matches lac lake, and the vermilion is rather more scarlet than artificial vermilion, and may either be cinnabar or the admixture of vermilion with a little red lead. If red lead has been used, it has not discoloured. There is also pure red lead which has discoloured in places, possibly suggesting that it is not mixed with vermilion in the other letters. The transparent copper green and possibly malachite occur among the greens.

English Missal. Add. 29704.—The next manuscript examined was an English Missal of the end of the fourteenth century. The ultramarine is very fine in quality, the lake matches lac lake, and the other pigments are red lead, vermilion, transparent copper

green, and soft low-toned greys and browns, probably obtained with earth colours.

This completes the typical English manuscripts which I have examined, those of the fifteenth century being mostly of foreign origin, but there are two manuscripts in the Advocates' Library, Edinburgh, which still remain to be described.

The next manuscript examined was the Culross Psalter, supposed to be of Scottish origin, and of the date 1470. The pigments on this seemed to be malachite, vermilion, a yellow about which I am not certain, and a fine quality of lake, but the main interest of this manuscript is the blue which is no longer ultramarine, but azurite. This is the first appearance on the British manuscripts we have examined of the very bright and beautiful azurite which is found on late fifteenth century manuscripts, and it continues through the sixteenth to the beginning of the seventeenth century. It is quite different in tint to the azurite found on the late thirteenth and early fourteenth century manuscripts to which reference has already been made. We do not know the place from which it was obtained, but we are told by Pacheco, the father-in-law of Velasquez, that azurite was getting rare owing to the conquest of Hungary by the Turks, and he mentions some being obtained from Venice. It is possible, therefore, that the origin of this fine azurite was some discovery of a new copper vein in Hungary. Azurite is found as a surface copper deposit, and as the mining operations are carried deeper into the earth, it disappears, so that we could expect to find that the supply decreases after a certain

length of time. If, however, Pacheco's statement is correct, the ultimate disappearance of azurite from the European palette may have been due to the presence of the Turks, and the old mines may have been lost during their period of occupation and never rediscovered.

Speculum Vitæ Christi. (18.1.7.) Advocates' Library, Edinburgh.)—This is an unusual manuscript both from the point of view of pigments and medium. In the first place it has been painted with two azurites of different tint, the one of a purplish shade which suggested at first that it must be ultramarine. The presence of these azurites would place the manuscript definitely in the latter half of the fifteenth century.

There is also a very beautiful lake which gives the reactions of madder. The question as to whether madder lakes were known in mediæval times is at present an open one, as although madder was known as a dye, and the preparation of a pigment from it was known in Egypt and in classical times, receipts for the preparation of madder lakes are conspicuous by their absence from monkish manuscripts. I have very little hesitation, however, in saying that this lake is madder lake of a fine quality, and that therefore we are justified in saying that madder lakes were being used at any rate in the fifteenth century. I have not found indications of madder lakes on earlier manuscripts.

Vermilion, orpiment and two shades of green are used upon this manuscript, and a fine pink which seems to have been obtained by mixing madder lake with white. Some of the green appears to be malachite, but there are some other portions of green which I

have succeeded in imitating exactly by dissolving verdigris in beeswax. The appearance of this green first made me suspect the presence of beeswax. There can be no doubt that at any rate a large portion of the painting is done with beeswax and not gum. The use of beeswax in this way involves the introduction of some volatile medium to dissolve it in, like turpentine. The earliest mention of the use of such volatile mediums are in mid-sixteenth century receipts for varnishes, but it is evident from this manuscript that spirits of turpentine or some similar medium must have been known and used by this illuminator at a much earlier date. I have not found on any other manuscripts another example of this use of beeswax.

On one of the pages there is what appears to be silver paint. In most of the old manuscripts where silver has been used, it has turned black, but in this case it has not done so. This may be due to the fact that it is not silver but tin foil which has been used, or possibly the use of the beeswax has preserved the silver from tarnishing.

Continental Manuscripts.

We now begin the consideration of the French, German, Flemish and Italian manuscripts which I have examined.

The first of these (Harley 2788) is a typical example of a Carolingian manuscript of about 800. The pigments used upon this correspond fairly well with those found on the early Irish manuscripts, the blue being badly washed ultramarine, red lead with no vermilion,

and orpiment as the yellow. The crimson colour, however, matches the Byzantine crimson and not the Irish purple, so that apparently the preparation used is the same as that found on Byzantine manuscripts, probably obtained from the Murex, and is not of native manufacture like that found on the Irish manuscripts.

Besides this, there is a dull green, earth colours, purple lake, and a white which is apparently white lead, though this is doubtful. With the exception therefore of red lead in place of vermilion, on the whole the pigments correspond much more closely with the Byzantine than with the Irish. This is specially shown in the use of earth colours which are often to be found on the Byzantine, but not on the Irish manuscripts.

This manuscript was examined simply with a view to seeing how far the same pigments are to be found on the Continent as we have already seen in Ireland and England.

Amiens Missal, 17742.—This next French manuscript is of considerably later date, 1218. It is painted with good ultramarine, but not of the finest quality; transparent copper green, a poor and faded lake and vermilion. The gold leaf used is in some places raised and burnished. It corresponds, then, fairly closely with the pigments used on English manuscripts at the same date.

The next manuscript examined was a French Psalter of the year 1260. (Add. 17868.)—This is a typical thirteenth century manuscript, the ultramarine being very fine in quality, and the lake exactly matching lac lake.

Somme le Roy, 28162.—The next manuscript examined belongs to the year 1300. This is interesting as having upon it the dark variety of azurite which has already been described in connection with the English manuscripts as coming in the late thirteenth century and lasting into the fourteenth, and as being specially characteristic of Flemish manuscripts of about this period. There are two blues on this manuscript. The more purple one may be ultramarine, but I am disposed to think that it is a darker shade of azurite, corresponding to the two azurites to be found on a manuscript in the Advocates' Library, Edinburgh (Speculum Vitæ Christi, 18. 1. 7), to be described later. It was, however, very difficult to come to a final conclusion on this point. Besides these, the other pigments are red lead, ultramarine ash, malachite green, vermilion, a poor faded lake, and the gold leaf is burnished and raised on gesso.

Poitiers Bible, 19. *D. II.*—The next manuscript is dated before 1356, and is known as the Poiters Bible. It was captured along with King John. This manuscript is painted with ultramarine, strong fine lake matched by lac lake, red lead, pale mixed green, which I was unable to identify, and vermilion.

XVII, E. 7.—This manuscript is painted with lac lake, vermilion, red lead, and a faded yellow which I was not able to identify, but which was probably orpiment, and the blue is either a mixture of ultramarine with azurite, or is an inferior quality of ultramarine very different from that which was found on other manuscripts of this period.

Harley, 4381. *French Berry Bible.*—The pigments

on this manuscript are ultramarine, vermilion, red lead, ultramarine ash, and lac lake. This is not given in the table.

Harley, 2897. *Burgundy Breviary*. — The next manuscript is known as the Burgundy Breviary, and the date is before 1419. The ultramarine is of very fine quality ; the lake is matched by lac lake, and the other pigments are red lead and vermilion, and a dull yellow, which is probably yellow ochre. This manuscript is, however, of great interest, as it is the first upon which I found finely crystalline verdigris, which is characteristic of the fifteenth century manuscripts.

The knowledge of how to prepare verdigris, by the action upon copper plates of fermenting grape skins, was known from the time of Pliny, but, up to the beginning of the fifteenth century, it will be noted that I have never been able to identify it on any of the manuscripts examined, although occasionally there have been greens which may have been verdigris poor in quality. With the opening of the fifteenth century, we find on the manuscripts a very brilliant crystalline verdigris constantly used in place of the transparent copper green which we find through the earlier centuries. Green seems to be a rare pigment on the fourteenth century manuscripts, and it is possible therefore that there may be a gap of a certain number of years between the use of the crystalline verdigris and the transparent copper green. This, however, is not likely, as this same green is to be found apparently on the early "oil" pictures of Van Eyck and his followers.

We have two problems to solve here. In the

first place, why the use of this green was replaced by that of verdigris, and in the second place, how the brilliant grass green colour of the verdigris used was obtained. In the first place I think it is open to question whether, although the receipt for making verdigris was known in the time of Pliny, it was prepared at all through these earlier centuries. It is quite true that the only way in which the transparent copper green can be imitated is by dissolving copper acetate in a pine balsam, but in the case of the German manuscript in the Advocates' Library, Edinburgh (Laing 5), which I shall shortly describe, one of the portions of the transparent copper green which I examined under the microscope showed the presence of partially dissolved blue crystals of azurite, thus suggesting that the mode of manufacture had been to treat azurite with vinegar, evaporate to dryness, and then dissolve in the pine balsam. The presence of this azurite is all the more puzzling as at the date of this manuscript (eleventh century) we do not find azurite being used as a pigment. It is possible, however, that an inferior azurite which was not considered good enough to replace ultramarine, was treated with vinegar and then dissolved in resin in order to make a fine grass green. Azurite treated in this way with vinegar would not be suitable for a green paint, as it is completely soluble in water and is not so permanent as the same product dissolved in pine balsam.

To come now to the fifteenth century verdigris. Verdigris is still, I believe, manufactured in France by the old method of packing copper plates along with

fermenting grape skins, although there are other chemical methods of manufacturing it which are more rapid and which are largely used. The verdigris sold to artists is usually the normal copper acetate, the true verdigris being basic and only partially soluble in water. If the true verdigris is treated with a little boiling water part is dissolved, and an insoluble basic salt is left, itself matching the fifteenth century verdigris. This would be a necessary process to prevent the soluble portion flowing beyond the painting. But this does not explain the whole of the problem, as granting that they had this greener green, it is quite evident, from the variety of the tints, that it has been mixed with some yellow. If we consider shortly the yellows that they had available—if mixed with orpiment it would turn black, and if mixed with yellow oxide of lead, the colour is also destroyed. The other available bright yellows are saffron and yellow lake, and if we are to assume that the reference in the Strassburg manuscript (Eastlake, Vol. I. p. 443) is to gamboge, we must include gamboge among the fifteenth century pigments. If verdigris is mixed with these three yellows and exposed to light, the saffron fades rapidly, the yellow lake fades next, and the gamboge is far the most permanent and also produces the most beautiful green. We may, I think, therefore exclude saffron and we are left with the choice between yellow lake and gamboge. Of these, I have detected yellow lake in green on a Psalter belonging to Henry VI. probably done in Paris, and dated 1430 (Dom. A. XVII. Brit. Mus.), and also on one of the Venetian Ducali (20196, f. III.) 1501–21,

so that yellow lake was used, but the peculiarity of these bright fifteenth century greens is that on examining through the microscope, in some cases I was unable to detect particles of yellow colour. If gamboge, which is of the nature of a stain, is used mixed with verdigris, it is impossible to detect the yellow particles of pigment, the result simply being a brilliant green in which nothing is visible except the crystalline structure of the verdigris.

I am disposed, therefore, to suggest, as a temporary hypothesis, that up to the fifteenth century the transparent copper green obtained by dissolving azurite treated with vinegar in a pine balsam was used, because in that way a fine pure grass green should be obtained, even the selected verdigris from the action of copper plates not giving all that was required, and that the use of verdigris in the fifteenth century may have been due either to the fact that it was only then that the conditions for making a fine green, not too blue in tint, were discovered, or because gamboge was now coming into the European markets, and for the first time, therefore, a yellow was obtained which, by being mixed with verdigris, would give the variety of grass green which was required and at the same time result in a pigment of sufficient permanency for work on illuminated manuscripts. Whatever the explanation may be, I have failed to identify with certainty verdigris on any manuscript that I have examined before the year 1400, while from 1419 onwards brilliant greens are to be found which, under the microscope, reveal the crystalline structure of verdigris, and do not always show the presence of a yellow pigment mixed

with the crystals, and which at the same time cannot be matched with the blue-green verdigris of to-day.

Dom. A. XVII. *Psalter, Henry VI.*, probably illuminated in Paris. Date 1430.—This is a typical fifteenth century manuscript. The ultramarine is fine in quality, the green is verdigris; ultramarine ash is used for greys, orpiment for yellow, and in this case there is evidently a certain amount of a yellow pigment, probably yellow lake, mixed with the verdigris to form a grass green vermilion. Gum has been used heavily in some parts, so much so that it gives rise to the suspicion that the verdigris has been dissolved in beeswax as in the case of the manuscript No. 18.1.7 in the Advocates' Library, Edinburgh, but on careful examination, I came to the conclusion that this was not the case.

Add. 35312.—The next manuscript belongs to the middle of the fifteenth century, and is again a typical example of fifteenth century work. Magnificent greens, obtained with verdigris, finest ultramarine, vermilion, red lead, and a pinkish lake are all used. The use of red lead so late as this is rather exceptional.

18. 8. 13.—The next manuscript examined is a French Book of Hours of the fifteenth century, of which the date is not known more accurately, in the Advocates' Library, Edinburgh. It is a typical example of late fifteenth century work, as we find here not only verdigris, red lead and vermilion and a very fine lake, but the lake is glazed over with vermilion in order to produce a rich crimson, and the blue is no longer ultramarine, but is the brilliant azurite which has already been described on the English manuscripts.

Besides the manuscripts already described, I have examined a certain number of Italian manuscripts, and the information derived from them will be found to confirm that already obtained from those of English and French origin.

Italian Manuscripts.

The earliest examined is an Exultet Roll (British Museum 30337) which contains very few pigments, and these considerably worn, but it is easy to identify on it ultramarine of medium quality, and very coarsely ground vermilion which is probably cinnabar. There is also gold paint and a pale green which I could not identify, but which seemed to be inferior malachite.

The next Italian manuscript is a Psalter from Monte Cassino of the twelfth century (18859). The ultramarine upon this is of very fine quality, but is probably burnished in the way already described. The other pigments are vermilion, transparent copper green, and orpiment, and a purplish lake mixed with white. Very fine decorative effects are obtained in this manuscript by painting orpiment and gold next to each other on some of the letters.

The next Italian manuscript examined is a Psalter at the end of the twelfth century (9350). The pigments are vermilion, orpiment, fairly good lake, and later on in the manuscript, the orpiment for painting the letters seems to have been replaced by yellow lake, which is faded. There are mixed tints and greens which I have not been able to identify. This manuscript is principally of interest as being the earliest example of

a European manuscript in which the ultramarine is perfectly prepared, and of the very finest quality. As will be seen by referring to the Byzantine manuscripts, the earliest date that we have had for a fine ultramarine is the ultramarine used in the earlier part of the twelfth century. (Egerton 1139, Queen Melissenda's Psalter). We now find it in this Italian manuscript, and at later dates still on French and English manuscripts.

Justinian's Institutes. (10. 1. 4. Adv. Lib. Edin.).—The next manuscript examined was Justinian's Institutes, in the Advocates' Library, Edinburgh, an Italian manuscript of thirteenth century script. The pigments in this are red lead, vermilion, lac lake, a dull green, and dull yellow which I could not identify, and the blue is dark azurite which we are familiar with in the late thirteenth and early fourteenth century manuscripts.

Perugia, 21965.—The next manuscript examined is one from Perugia. The ultramarine is good ; the other pigments are vermilion, red lead, orpiment, a pinkish coloured but very bright lake, and the transparent copper green. There is also a certain amount of a crystalline green which is possibly malachite, but I was not able to identify it with certainty.

22497.—The next manuscript examined is also from Perugia of about 1400. This manuscript is painted with vermilion and with the dark blue azurite already described. This is a late date to find the dark variety of azurite, and it would be interesting to know whether this manuscript should not be placed a little earlier.

Florentine Missal, 14802. 1457.—This is a typical manuscript of the early fifteenth century. The blue is

ultramarine, the green fifteenth century verdigris, and the other pigments are vermilion, red lead, orpiment, and a very fine pinkish lake.

21463.—The next manuscript is one of the Venetian Ducali, date 1486. This manuscript is interesting on account of the fine crimsons which we now find common to late fifteenth century manuscripts, produced by glazing over vermilion. This is a dull green which I could not identify, and the blue is ultramarine, thus overlapping a little with the use of the late fifteenth century azurite which we have found on other manuscripts.

Egerton, 754.—This next manuscript is also one of the Venetian Ducali, dated 1534. It is painted with the brilliant fifteenth century azurite, and the green is fifteenth century verdigris,

Egerton, 755. 1538.—The next Ducali examined has again the brilliant crimsons produced by glazing the fifteenth century verdigris and the late fifteenth century azurite. We also find here the brilliant mauve colour which is found so commonly on sixteenth century manuscripts, and a description of it is given in the chapter dealing with the English legal rolls.

20916. 1539. 45.—This again shows the beautiful fifteenth century azurite in fine perfection.

Flemish Manuscripts.

I have recorded the examination of very few Flemish manuscripts, as there is nothing very special to say about the late fifteenth century ones as far as the pigments used are concerned. The first I examined is a Flemish Psalter of the date 1230–50 (2. B. III.), and it is

interesting because it is painted with the dark variety of azurite already described, a certain amount of black having apparently been introduced for shading the blue. The other pigments are lac lake, vermilion, red lead, and a crystalline green which seemed to me a little deep for malachite, and is the only case I have come across where I was disposed to think that a poor quality of verdigris had been used on one of these early manuscripts.

18. 7. 18. Adv. Lib. Edin. Hours.—The next manuscript examined is in the Advocates' Library, Edinburgh, and is a Book of Hours of the fifteenth century. The pigments are typical late fifteenth century pigments consisting of the fine fifteenth century azurite already described, and a mixed green which is fifteenth century verdigris, and a very fine lake, and glazings of lake over vermilion.

German Manuscripts.

I have examined a couple of German manuscripts. The first (Gospels, Laing 5, Ed. Un. Lib.) is in the University Library, Edinburgh, and is very interesting. From the script these Gospels are supposed to be eleventh century. The decorations are of a very crude description, and I have been able to identify among the pigments, vermilion, red lead, transparent copper green, badly washed ultramarine and a very poor lake. There is also a dull orange coloured yellow, which I have not been able to identify. The badly washed ultramarine would certainly make this an early manuscript. It is also of interest because the gold is

burnished and raised on bole, and if therefore the date of this is correct, it is the earliest example of burnished gold on bole which I have found. The transparent copper green is used very freely, and it was in a portion of this green that I detected the crystals of azurite, apparently converted into the transparent non-crystalline green which I have already referred to on pages 35–38, in discussing the question of the use of verdigris in the fifteenth century.

The next German manuscript examined is a thirteenth century manuscript (17687). This is painted with the dark variety of azurite, a dull purplish lake, a dull green which is apparently a poor quality of the transparent copper green, vermilion, and the gold leaf is burnished and laid on bole. It thus corresponds in the date of the use of azurite with the Flemish, English, and Italian manuscripts already described.

I have grouped these manuscripts in describing them according to countries, and therefore it is a little difficult to follow how far the changes of palette which are found through the centuries in one country agree with the changes in the others, but it will be seen that I have tried, as far as possible, to deal with all the more interesting points. If, however, the table upon which the results of this examination are summed up is examined, it will be found how very closely the changes of palette agree in different countries as we move through the centuries. Certain pigments remain common throughout the whole of the period dealt with, namely gold, vermilion, red lead, and orpiment, and to these we might perhaps add malachite, which, whether in the form of a natural copper

carbonate, or an artificial preparation (and it is very difficult to distinguish between these unless a portion can be separated for examination) appears again and again at various dates. I have found artificial malachite on an Italian musical scroll, which, from its decoration, and from the presence of azurite, must belong to late fifteenth or early sixteenth century. If we proceed to consider how far different pigments are associated with different countries, we find that the use of the purple dye from the murex is peculiar to Byzantine manuscripts from the earliest times up to the date of the sack of Constantinople by the Crusaders, but we also find it on manuscripts about the date 800 in Europe and we also find a corresponding purple on earlier English and Irish manuscripts, and the use of this purple remains peculiar to Irish manuscripts up to the thirteenth century, while very rarely appearing on those of England.

The next pigment which is worthy of consideration is ultramarine. As we follow the history of ultramarine through the centuries, we find that in the early centuries it is badly prepared on all manuscripts, and that this inferior preparation of ultramarine continues on both Irish and Byzantine manuscripts, in the case of the Byzantine manuscripts there being only one exception among those examined, the quality getting even worse after the sack of Constantinople. On European manuscripts, however, there is a steady improvement in the washing of ultramarine, until at about 1200 we begin to get ultramarine of fine quality, and from the thirteenth century onwards, with one or two rare exceptions, the ultramarine is always beauti-

fully prepared on all the European manuscripts. We can get a rough idea, therefore, of the date of the manuscript if it is not of Irish or Byzantine origin, from the condition of the ultramarine as it appears under the microscope.

With the coming in of properly washed ultramarine, we find ultramarine ash being used for painting delicate back-grounds. The earliest date upon which I have ultramarine ash recorded is in the thirteenth century. (Somme le Roy. 28162.)

The next pigment which is worthy of consideration is azurite. Although azurite was known to Pliny, I have not detected it on any manuscript, with one doubtful exception (Vesp. A. 8.) until about the middle of the thirteenth century, and we find a dark blue azurite being used, and continuing into the fourteenth century. I have found no instances of azurite in the first half of the fifteenth century, but towards the close of the fifteenth, a very brilliant azurite comes into use, quite different in appearance from the earlier one already described which is found on late fifteenth, sixteenth and early seventeenth century manuscripts.

Among greens, I have already referred to malachite. The other two greens of interest are verdigris and the transparent copper green which I believe I have been the first to describe, and which we find common to manuscripts of all countries from the eighth to at any rate the middle of the fourteenth century, if not later. This is replaced early in the fifteenth century by a brilliant verdigris which continues to be the principal green in use during the fifteenth and sixteenth centuries, the transparent copper green never being seen again.

The lakes deserve a word or two. They are of course very difficult to identify, as they are made from such similar substances, but there can be no doubt about the common type of lake used in the late thirteenth and fourteenth centuries, which is matched by lac lake, and which is found over and over again, nor can there be any doubt about the use of madder lake, at any rate on the later fifteenth century manuscripts—a lake much more brilliant than anything that has been used at earlier times.

The only pigment not mentioned now is gold. The use of gold leaf and gold leaf ground down into gold paint is found from the earliest to the latest times, but the use of raised burnished gold letters on bole seems to come in towards the close of the twelfth century, the only exception that I have seen being the eleventh century German manuscript which I have described, and which is in the University Library of Edinburgh. (German Gospels. Laing 5.) This would be a very easy date to fix by examination under the microscope, and would be a very useful one. The only other use of gold which I have described, and which I believe is new, is the coarse apparently river washed gold dust which I found on three English and one Irish manuscript from the eighth to the early eleventh century. It will be of interest to search further for other manuscripts containing similar gold. I have not seen any out of the British Islands, and I have not found any examples at a later date. It should, therefore, be another useful method of identifying and fixing dates.

If this summary, therefore, of the results is compared

with the table, it will be found that the pigments used give a good deal of information both as to the source of a manuscript, and also as to its date. Doubtless the examination of a still larger number will enable these points to be fixed with even greater exactitude than has been possible in the preliminary survey which I have been able to make of the whole of this subject.

CHAPTER VI.

EXAMINATION OF VENETIAN DUCALI AND CORAM REGE ROLLS.

In the Manuscript Department of the British Museum there are a large number of Venetian Ducali. The earliest of these is between 1501 and 1521, and the latest, which I have examined, is 1700. These Ducali are adorned with coloured illuminations, and thus form a connecting link with the Missals though at the same time they are carried on to a later date, and have the advantage of being documents of which the date is known with approximate correctness. One or two of these have already been described.

The first of the additional ones which I examined is No. 20916, fol. 3 (1501–21). This manuscript is painted with a very fine azurite; vermilion with lake glazings; gold used as a pigment as was customary in the fifteenth century illuminated manuscripts, and verdigris which contains little pieces of azurite. This admixture of azurite with verdigris also occurs in the sixteenth century legal rolls and seems to be a peculiarity of this time, as I have not noticed it in the verdigris used in the fifteenth century.

I have already discussed the question as to the bright green obtained with verdigris in the fifteenth century, and have stated that the verdigris must have been mixed either with gamboge or with a yellow lake. In the case of this document, particles of yellow lake can be seen towards the edges of the green, while separate crystals of verdigris can be detected which have the green colour which belongs to the washed pigment already described. In the main mass of green, these separate particles of lake are not visible, but the general staining effect is present, thus producing the grass green tint.

On this manuscript is also to be found a very delicate mauve, which evidently consists of a white, a blue and a lake mixed together, as particles of lake can be detected, and particles of the blue. At first I was disposed to think the white and blue was ultramarine ash, and very beautiful results can be obtained by mixing ultramarine ash directly with lake, but on close examination, I am disposed to think that the particles of blue are azurite mixed with a white, thus agreeing with the methods which will shortly be described as being so common in the sixteenth century legal rolls, where both white lead and azurite have been found. There is therefore nothing in the pigments used here which differs from those already described as belonging to the late fifteenth century period.

Folios 4, 5, 6, 7, 8, 10, and 11 all belong to the earlier part of the sixteenth century. The pigments on ff. 4, 5, and 6 are exactly the same as those on f. 3, while ff. 7 and 10 contain the same pigments with the addition of orpiment, and f. 11 contains the same

pigments with orpiment and a very rich lake, especially fine in quality, and which can, I think, only be madder lake from its appearance. Folio 8 was too soiled for successful examination, and f. 9 (1570) was also very dirty, and had a different blue from the others which, had it not been for its early date, might well have been an artificial copper carbonate and not azurite. It might also, however, be a very poor sample of azurite, but it would be impossible to settle this question without the removal of a minute particle for examination under the microscope by itself.

In folio 12 (1559–67) the same pigments occur, *viz.* verdigris, orpiment, and a pinkish coloured lake, but the blue is again very poor in quality, and resembles very closely an artificial copper blue.

We thus have here two manuscripts, the one dated 1570 and the other 1559–67, in which it is quite possible that an artificial copper blue occurs. As we have seen in the case of the legal rolls, no such case of artificial blue occurs until the seventeenth century, and therefore it is improbable that these blues are anything but poor azurite. It is unfortunate that this question cannot be finally settled under the circumstances, and it is quite possible, of course, that the artificial blues overlap with the use of azurite, and they may have been known as early as this date. It would be a matter of considerable importance to try to settle this point by means of documents from which small particles can be removed for definite identification.

The next document examined was No. 18000 (1521) painted with azurite, a weak yellowish green which it was impossible to define, a very fine lake, almost

certainly madder, and a beautiful mauve. There are some very fine letters painted with verdigris, vermilion, gold paint, and a greyish white.

The next document was No. 15518 (1531), which was painted with vermilion, lake, azurite, verdigris, mauve, and orpiment.

The next, Eg. 755 (1538) was painted with verdigris, azurite, fine lake, vermilion, mauve, and a yellow which it is difficult to define.

17373 (1554) contains azurite, verdigris, gold pigment, lake, and orpiment. On this document no mauve had been used.

Kings 156 (1568), was painted with azurite, a very fine lake, the same mauve as already described, gold used as a pigment, and a yellow which I identify with gamboge.

16996 (1587), is painted with azurite, fine lake, weak greenish yellow, not identified, shaded gold, and soft brown tints, which might well be made of some brown earth colour such as brown ochre or umber. This is the first case in which I have found these soft browns introduced upon these documents.

23970 (1603). The yellow used here is weak and it is impossible to speak with certainty as to its composition. The same soft ochre browns occur as in 16996; the green is verdigris with the particles of blue mixed with it as already described and the blue was a fine quality of azurite.

17348 (1613). This was also painted with fine azurite, a little lake and soft brown.

17349 (1613). A very dark dull mixed blue used on the dress of the Virgin cannot be identified, and a

very thin wash of blue on the cupids' wings was too thin for identification. A fine lake has been used, and the lion looked as though it had been painted in red lead which had turned black. It was impossible on this document to identify any of the pigments with certainty.

Eg. 759 (1635) is painted with vermilion, very fine lake, shaded gold, and azurite.

Eg. 760 (1643), Azurite, very fine lake, and shaded gold are used.

Eg. 761 (1644), Verdigris, azurite, fine lake, and shaded gold.

15131 (1647), Azurite, verdigris, probably gamboge, vermilion, fine lake and shaded gold.

There now comes an unfortunate gap in the sequence of documents in the British Museum, the next manuscript being No. 15140, which is dated 1700. On this the blue was certainly an artificial copper blue.

It will be seen then that with two doubtful exceptions, which may be due to an inferior azurite having been used, the pigments on the Venetian Ducali from 1500 up to 1647 are the same as those found on the fifteenth century Missals, and that the use of azurite continues up to that date. This is some twenty years later than its disappearance from the English legal rolls. This, however, is quite conceivable, as Venice, being the great commercial centre, may have been able to obtain or to have stores of azurite longer than countries so far from the sources of supply as England. It is unfortunate that its disappearance between 1647 and 1700 cannot be decided by means of these Ducali in the British Museum.

I also examined one or two other documents. There is a miniature (No. 22494) showing the reception of the Siamese ambassadors by Louis XIV. in 1686, in which the blue used is an artificial copper blue. There is also a very interesting 16th century picture of water-birds, which has been painted by hand (6485) on which azurite is used.

A eulogy on Henrietta, Daughter of Charles I. (33572) supposed to have been written about 1661, and the blue used is ultramarine, and therefore is no use for the purpose of fixing the dates at which azurite is replaced by artificial copper blue.

It is interesting to note that although smalt was certainly being used as a blue by painters from the latter half of the sixteenth century onwards, it does not occur on any of these documents.

The Coram Rege Rolls.

In the last chapter, I completed the description of the pigments used in illuminated missals to the close of the fifteenth century. I now propose to continue the history of pigments by the account of those used on a series of dated documents of undoubted authenticity. The Legal Rolls preserved in the Record Office were formerly recorded on long strips of parchment, sewn together at the top, and from about 1500 to about 1700, the first page was adorned with gilt letters and painted miniatures.

These painted miniatures have never been retouched in any way, and must each have been painted in the year to which the roll belongs, so that they

form a unique series of dated documents without a break.

(1013.)—The date of the first of those examined is 1515. The initial letters on the first page are burnished gold leaf on gesso just in the same style as the illuminated Missals, and at the head of the page is a miniature of the King on his throne. At the back of the King's throne, the parchment has been covered with a yellow ground over which gold paint has been laid. This coat of yellow is very thin, and difficult consequently to identify, as it might either be a very fine yellow ochre, or an orpiment which has become dull and dirty with age. The result of my examination was to decide ultimately, though not conclusively, in favour of orpiment. As we shall see, both fine yellow ochre and orpiment were used on subsequent rolls.

The green in this picture is undoubtedly verdigris but has one peculiarity which I have not noted on any fifteenth century manuscript, and that is the mixture with it of particles of azurite. This raises the interesting question whether this green was not prepared by the direct attack of azurite with vinegar instead of by the corrosion of copper. I have already discussed the various tints of verdigris which can be made by modifying the conditions of manufacture, and also the yellows available for mixing with it.

Some of the crystals seen here were not different in tint from modern verdigris, yet the green as a whole was nearer grass green and there were distinct indications of a yellow stain, but I could not find any separate particles of yellow lake.

As we shall shortly see, I found yellow lake in the green of a subsequent document, and it may have been used in this case also. The choice lies between yellow lake and gamboge.

Vermilion and ultramarine have been used for the scarlets and blues. The most interesting colour on this manuscript is, however, a mauve which is to be seen on the King's robe. This mauve is a favourite colour in subsequent manuscripts, and I have also found it on some of the Venetian Ducali. In the chapter on early English manuscripts will be found two examples of the occurrence of mauve, but it is certainly rare, as far as my experience goes, on documents before the sixteenth century.

This mauve can readily be obtained by mixing ultramarine ash with lake, but careful examination showed that the mauve on Henry VIII's robe was a mixture of white lead, azurite, and lake.

(1012.)—This Roll, of the same date, is very similar in the pigments used, though apparently azurite is entirely absent; the blue is ultramarine, and the verdigris green is free from particles of azurite and resembles more closely the fifteenth-century verdigris. Vermilion glazed with lake is used, and gold paint, and the delicate greys are apparently ultramarine ash, while white lead is used on the robes of the attendant lords.

(1126.)—The next Roll examined is dated 1543. There is no ultramarine on this or any subsequent roll, the blue used being azurite. In the decorative portion, there is a curious mixture of raised burnished gold letters, and of gold paint coarsely laid on, while

the blue associated with the coarse gold-paint decoration does not seem so fine as that on the miniature. There can be no doubt, however, that it was all done at the same time, and Dr. Shaw tells me he has seen many similar examples of the mixed use of gold.

Mauve again occurs in the canopy, and yellow ochre is apparently the pigment over which the gold paint is laid in streaks. There is a fine crimson lake in the King's robe which is matched by lac lake.

(1185.)—The next roll examined is dated 1558. The blue is azurite, while there are delicate mauve grey backgrounds of which the basis may be ultramarine ash. In the canopy, owing to some chemical action, the azurite has largely turned green, with bits of unchanged blue still in it. The whole appearance suggests that the original was azurite. This is the only case I have found of azurite changing, and it is worthy of further investigation to find out the conditions causing such a change.

The verdigris in the miniature has again azurite mixed with it as in Roll 1013.

The pavement consists of green tiles which are so painted as to give two tints of green to each half of each tile. As far as can be judged under the microscope, the green is of exactly the same tint over the whole tile and then one half has been varnished faintly with an excess of gum so as to produce the effect.

(1450) 1616.—The blue on this miniature is azurite, but the green is no longer verdigris. It is a copper carbonate and is apparently artificial and not malachite. There are two yellows used on this miniature. The pear-shaped ornament is orpiment shaded with lake,

while the ground in front of the cushion is yellow ochre. Probably the yellow round the canopy is also orpiment. The use of gold on gesso for the letters has now disappeared. The yellow round the throne is over-painted with gold.

(1499) 1621.—The blue on this miniature is azurite and the green is artificial copper carbonate, while mauve occurs as before, and there is gold paint over yellow on the arms of the king's chair, and an ochre on the rim of the canopy. White lead is used to paint the ermine.

(1537) 1625.—This miniature is of exceptional interest as the blue upon it is no longer azurite, but blue verditer. The green is the artificial copper carbonate and mauve effects are used as before. More than one tint of yellow occurs, but they are none of them orpiment, and are apparently yellow ochre.

(1562) 1629.—The blue in this miniature is also blue verditer, while the other pigments are the same as in 1537.

(1826.)—This roll is of the date 1672. The portrait is apparently painted in oil, the surrounding decorative treatment being in a different medium. There is ochre under the gold in the scroll of the letter P, and the blue is blue verditer.

This series of rolls is of great interest as showing the gradual deterioration of the traditions of the fifteenth century illuminator. It is not my business here to discuss their artistic merits, but the gradual change in the palette. This change in the palette, however, is not without its decorative significance.

As I have shown in the earlier chapters, the beautiful surfaces of the illuminated manuscripts is largely due to the use of coarsely ground crystalline pigments.

At the beginning of the period discussed, the palette is the same as that of the fifteenth century, but in the seventeenth century we have first the replacement of verdigris by the non-crystalline artificial copper carbonate, and then the replacement of azurite by the weak and inferior blue verditer. I have already discussed the reasons for the disappearance of azurite from the artist's palette, and these documents give us a definite date as far as England is concerned. In Venice, as we found, its disappearance is somewhat later.

When it was no longer available, those engaged in illuminating work should have returned to the use of ultramarine, which was still in use among painters, but in the degraded condition of the art preferred the cheap and inferior blue verditer.

The most important fact in the history of pigments which is brought out by the enquiry into this period, from 1500 to 1700, is the disappearance in 1625 of azurite from the artist's palette which had been reintroduced as a pigment about 1470. It was just about this time that De Mayerne was writing, and he describes both pigments.

The presence of azurite in a picture may be regarded therefore as absolutely establishing the fact that it has been painted before the middle of the 17th century, while the probability is in favour of its being later than 1470.

The replacement of verdigris by artificial copper carbonate at the beginning of the seventeenth century is also of interest, though verdigris was, of course, used in painting long after this. This may, however, mark the earliest date when the artificial green copper carbonates came into use, to be so soon followed by the artificial blue copper carbonates or blue verditer.

I have in my possession one sheet of an old Italian choir book on parchment in which both azurite and green artificial copper carbonate occur as in No. 1450. Unfortunately there is no means of dating the document, and further evidence is required for finally establishing this date. It is, however, highly probable that the two verditers, blue and green, were introduced about the same time.

CHAPTER VII.

EXAMINATION OF PIGMENTS ON PICTURES OF VARIOUS DATES.

BEFORE beginning to describe the examination of pictures at the National Gallery, Edinburgh, and elsewhere, it is necessary to review the position as to the pigments used based partly on literary evidence, and partly on the result of the examination of illuminated manuscripts.

The question of mediums used will be discussed in a subsequent chapter, and therefore will be only briefly referred to here in passing.

Various pictures which I have had an opportunity of examining belong to the fifteenth century.[1] They are :—Picture in the National Gallery, Edinburgh, of a Madonna and Child belonging to Sir Thomas Gibson Carmichael ; a German panel picture which is also probably fifteenth century, of Saint Christopher. A fifteenth century picture of the Procession to the Cross, belonging to the Hamilton Bruce Collection, and the fifteenth century panels in the Director's Room in the Edinburgh Museum.

In the former examination of the illuminated manuscripts the pigments at the command of the fifteenth century artist have been pretty completely determined, Besides the earth colours which do not require special consideration, we have real ultramarine and azurite for the blues ; verdigris for green ; orpiment and yellow oxide of lead, yellow lakes and possibly gamboge for yellows ; vermilion and red lead for scarlets : Kermes, madder and lac lakes ; and ultramarine ash for soft grey.

It has already been noted that the green found in the later manuscripts and apparently made by dissolving copper acetate in a liquid balsam, is not found on the fifteenth century manuscripts, being replaced by verdigris, and I have discussed elsewhere how this bright green grass was obtained from verdigris. With the disappearance of the transparent green made by dissolving the copper acetate from illuminated manuscripts, we find in the fifteenth century a similar green appearing on "oil" pictures, again to disappear in due time.

As I have already stated, there is no receipt to be found for a green of this description earlier than De Mayerne's manuscript, which belongs to the early half of the sixteenth century, and where it is proposed as a green varnish for glass ornaments. One of the most interesting questions therefore in the history of painting is when this green ceases to be used. On this point, by the examination of the pictures in Edinburgh, I have not been able to obtain very much light, and it will require further investigation.

If we now examine the list of pigments in the table

compiled from literary sources, it will be noticed that the greatest changes which take place after 1500 are to be found in the blues. In the first place, some time in the first half of the seventeenth century, the use of azurite disappears. According to Pacheco this blue was getting rare owing to the conquest of Hungary by the Turks, which took place in 1526, and he tells a story of Titian giving Michael Coxis some azurite to assist him in copying the Van Eyck in Ghent.

De Mayerne describes two blues, one of which he states to be an artificial copper compound, and the other to be prepared from an Indian stone, and adds that he himself has prepared some from the stone in question. This is probably azurite, although his description is not very clear, and the two dates in the De Mayerne manuscripts are 1620 and 1636, while De Mayerne died in 1655. The receipts for artificial blue copper carbonates are very old, but they do not seem to have been used, at any rate in large quantities, until the sixteenth and seventeenth centuries. It is impossible to come to exact conclusions on this point by literary evidence, as a variety of names are used for these copper blues, such as Mountain blue, Ash blue, Bice and Verditer, and it is impossible to tell to what these names refer. It becomes therefore of considerable importance to decide the dates at which azurite finally disappears, and the artificial blues replace it.

The next blue of importance, which probably came into use in the latter half of the sixteenth century, is smalt. I have already given on page 12 such literary information as we possess as to the first production of this

colour. In 1704–1720 we have the accidental discovery of Prussian blue by Diesbach, and in a pamphlet 1733 Prussian blue is described, but is evidently regarded with some doubt as a useful pigment for painters.

It will be seen, therefore, that from the point of view of the history of pigments, after 1500 the two points of interest are the disappearance of the green which we may call the Van Eyck green, and the disappearance of azurite and the gradual introduction of these other blues, and in addition the introduction of green verditer. If these dates can be fixed with any exactness, they will be of considerable value in dating pictures. On this point the evidence from the Coram Rege rolls is valuable. Green verditer first appears soon after 1600, and blue verditer in place of azurite in 1636.

In the list of pigments given by De Mayerne, we do not find any great change on those already described, nor does any great change take place until the close of the eighteenth century, when, as will be seen by the table from literary sources, several new pigments were discovered. In the matter of yellows, reds, and lake there is nothing new.

The first picture I examined with the view of finding what blue had been used in painting it was the Madonna and Child in the National Gallery, belonging to Sir Thomas Gibson Carmichael. This is a very nice example of a tempera picture. It is in good condition, is free from varnish, and with the possible exception of the red lake on the robe, seems to be quite free from repainting. The medium is pure tempera, and the blue is a mixture of ultramarine

and azurite. We shall find one or two other examples of these two blues being mixed together. It may have been done possibly with a view to economy, the azurite being a cheaper blue than the ultramarine, or in order to get a slightly different tint than was obtainable with the ultramarine alone.

The next picture examined was the German panel which is evidently of northern origin, and has all the appearance of being late fifteenth century work. Here again, with the possible exception of glazings of lake on the red robe, the picture seems to be absolutely untouched, and both the medium and pigments are in the fine state of preservation, which one associates with the early "oil" pictures. There is a fine green on this robe, not quite so bright, perhaps, as the Van Eyck green, but probably of the same origin.

The significance of the presence of this green will be discussed when dealing with the subject of early "oil" mediums. The blue in this picture is ultramarine.

The fifteenth century panel picture which has been repainted to a certain extent, at a later date, in the Hamilton-Bruce Collection, deserves a more detailed description.

The picture represents the Procession to the Cross.

The sky, hills, castle, and procession to the Cross are all fifteenth century work, being painted in tempera, and in the sky and the figures, the blue used is azurite, which was used from about 1470. The three trees and the foreground in front of the big tree with the figures on it, have been retouched in oil, and are

apparently late eighteenth century work, judging by the pigments used.

Throughout, retouching in oil has been done, more especially in the foreground in front of the procession. The figure of a man leaning against the tree and a boy in the foreground have also been largely repainted in oil.

For our present purposes it will be noted that the blue in the original picture is azurite.

The fifteenth century panels in the Edinburgh Museum will be dealt with again more fully in discussing the question of mediums, but in the meantime it may be noted that the dark blackish-green robe from which the portion examined was taken, is covered with a very dark brownish-yellow varnish, lying underneath which is a fine blue which is also azurite.

In the case therefore of these fifteenth century pictures we have found either ultramarine or azurite or both blues used, and nothing else.

With reference to the date when azurite was first used, it must be noted, as already stated in the account of the illuminated manuscripts, that this blue seems to have appeared and disappeared at different times in the history of painting, and that there is a considerable gap between its last appearance on early fourteenth century manuscripts, and the appearance of a new variety of azurite, very fine in colour, about 1470. It is, however, described by Cennino Cennini, and it cannot be taken as absolutely proved that it was unused between these periods, but in the meantime, until there is further evidence, we may take its presence to show that the work at any rate belonged to the latter half of the fifteenth century.

The next picture in order of date which I examined is the panel portrait of a lady in the Hamilton Bruce Collection. Judging by the costume, this picture belongs to the close of the sixteenth century, and has the following inscription on it :—"Marguerite Foussar, Fem. de Misire Rene des Bois." It is very probably Flemish work, as most of the painting at that time was done by Flemish artists. This picture is fully discussed from the point of view of mediums later on, and in the meantime all that is necessary is to note that this is the first case in which I have found smalt used as a blue, in the muslin collar.

In the case of the pictures which are next to be described, unless there is a date on the picture, the method I have adopted is to take the date when the painter was born, add twenty years to this, take the date when he died, and date the picture halfway between when he was twenty and the date of his death. Where an actual date is on the picture, of course that is mentioned.

The first seventeenth century picture which I have examined is by Francesco Furini. It is entitled "A Poetess" (No. 64) and consists simply of a head and shoulders. This is an interesting picture, having been painted on several sheets of paper pasted together to form a kind of millboard, which has then been mounted on a thick, coarse, wood panel. A little of the paper examined under the microscope shows that the fibre is flax. The picture is in good condition, and is at present covered with a heavy varnish and has fine square cracks. The blue contains both ultramarine and azurite, so that this brings the use of azurite as

late as the first half of the seventeenth century, and is again an example of the mixture of the two blues together which we found in the earlier picture.

The next picture examined is by Dirck van Deelen (3) and therefore represents the Dutch School of landscape painting at very nearly the same date as the picture just described. This picture is dated 1644, and represents a lofty hall decorated with coloured marbles. The blue in this picture is ultramarine.

Next on the list we have a woody landscape by Hobbema (4). It is dated 1659. The blue used is again ultramarine.

The next picture examined is by Karel du Jardin—"The Farrier's Shop" (No. 26). It has a dark blue sky and bright white clouds. This sky is painted with blue verditer. The cracks are irregular in shape, and much broader and deeper than those which appear in any of the earlier pictures which have been described, and certainly suggest the use of a medium containing much more oil and less varnish. This is the earliest date at which the use of blue verditer has been found.

The next picture examined is by Ludolf Bakhuysen (No. 105), representing a Dutch lugger running for the entrance to a harbour. In this picture the cracks are square, and the picture is in excellent condition. The blue in the sky and on the flag is real ultramarine, while the pink on the flag has been retouched with lake in oil, judging by the way in which it has wrinkled in drying, as the lake crosses the old cracks.

It will be noted that the evidence from these seventeenth century pictures shows that ultramarine

was very largely used, especially by the Dutch School, and that the latest date at which azurite is found is the picture by Furini (1637), while the earliest date at which blue verditer has been found is the picture by Jardin (1660). These results suggest that the disappearance of azurite and the use of artificial copper blue in its place occurred somewhere about 1650. A picture by Teniers (28) is painted with smalt.

All these Dutch pictures suggest a similar technique, and from their appearance under the microscope, the surfaces being hard and polished, and the square cracks, suggest the use of a considerable quantity of varnish in the painting, the only exception where the technique seems to be different being the picture by Jardin.

The first picture belonging to the eighteenth century which was examined, is by H. F. Rigaud. "Portrait of Louis XV as a Baby." As Louis XV was born in 1710, the date of this picture must be about two or three years afterwards. The picture is in excellent condition, and is painted on one of the coarse canvases with a heavy priming similar to those used by Watteau. The cracks run in straight lines, and meet at an angle of about 60°. The sash of the baby and pillows upon which he is sitting are pure ultramarine of a very rich and fine quality. The other pigments seem to consist simply of yellow ochre and vermilion glazed with lake. The colour of these glazings is finely preserved.

Closely corresponding to this picture in date is a picture by Watteau (No. 59), "Shepherdess examining Bird's nest." This is a very fine little Watteau, and

the blue in the sky is a very good example of his rich and beautiful blues. An examination of this blue reveals the fact that it is an interpainting of verdigris with real ultramarine. Both are in perfectly good condition, and there is no sign of any blackening of the verdigris, while the working in of the green with the blue explains the peculiarly rich result which is to be associated with Watteau's blues.

The next picture examined is Madame Pompadour (No. 46) by Francois Boucher (1731–64). The blue dress in this picture is painted with blue verditer.

It will be seen therefore that the evidence from these pictures confirms the evidence from the legal rolls and the Venetian Ducali, azurite disappearing from the artist's palette in the early part of the seventeenth century and being replaced by blue verditer; the remaining blues in common use from 1650 onwards being ultramarine, blue verditer and smalt. The results also show that in the fifteenth and early sixteenth century mixtures of azurite and ultramarine were not uncommon.

Watteau is the only artist I have so far found getting rich effects by the interpainting of verdigris and ultramarine.

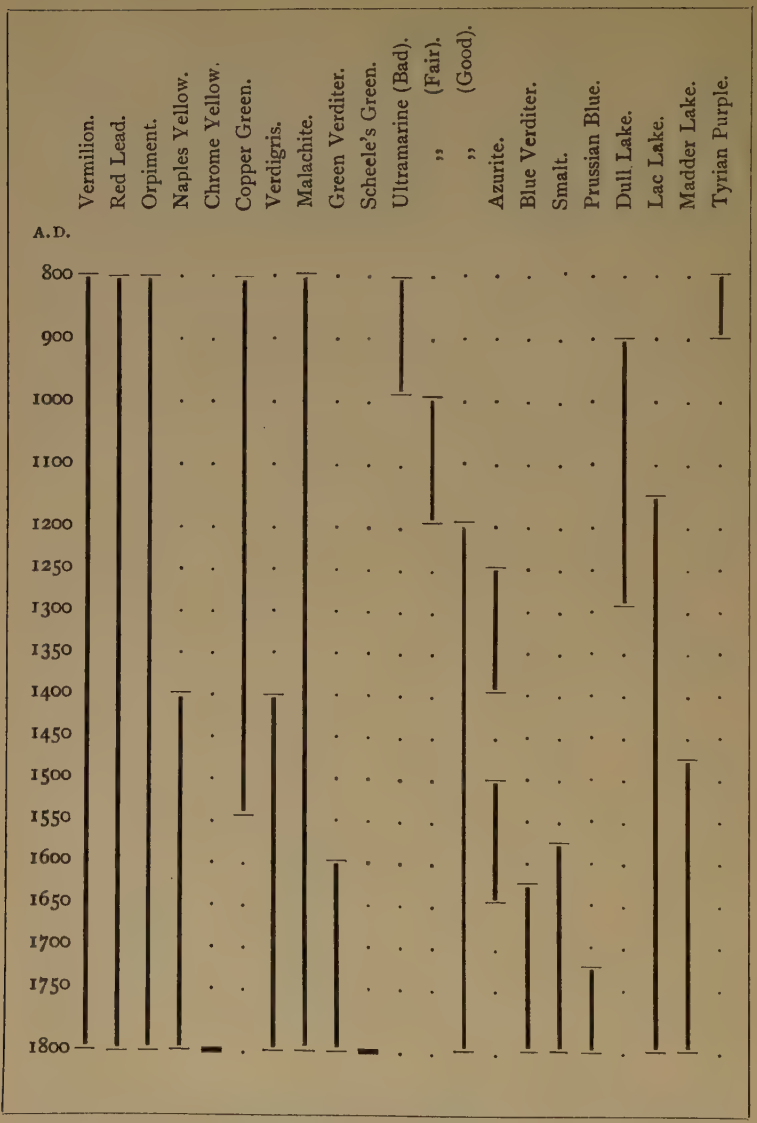
I have not so far come across a single example of the use of Prussian blue in the eighteenth century.

It will be seen that the results obtained from the examination of these pictures confirm those already obtained from the examination of illuminated manuscripts and the Coram Rege Rolls, as to the dates when certain pigments went out of use and others came in to replace them. In addition, we have

obtained the date of the first appearance of smalt, from the examination of the picture in the Hamilton Bruce Collection, which must have been painted somewhere about 1600, thus agreeing with the conclusion already arrived at as to the probable date of the appearance of smalt in the latter part of the 16th century.

In the following table, the conclusions obtained by this enquiry are summarised from the year 800 to the year 1800, so as to make the results easy for reference. I have included two modern pigments in this table, viz.: Scheele's green and chrome yellow, as they were both discovered in the closing years of the eighteenth century, though there is no evidence that chrome yellow was actually used and sold until early in the nineteenth century. I have not introduced into this table any reference to zinc white. Although it was certainly discovered in the eighteenth century as suitable for a pigment, I have not found any definite evidence that it was used by artists.

While doubtless further enquiry would enable many of these dates to be fixed with greater exactness, the evidence accumulated is sufficient to enable one to approximately date many pictures if they happen to fall within certain periods when changes were taking place in the artist's palette. In addition, further information can be obtained from the mediums used, which I shall proceed to discuss in the subsequent chapters. But two interesting examples have already been referred to where the dates were not known and where the mediums have proved of value in enabling the dates to be fixed. One is a



Note.—The date of the pigments used in Byzantine and Irish Monasteries is not included in the table.

sheet from an old Italian choir-book to which I have already referred, and in which the presence of azurite and green verditer side by side points to a date early in the seventeenth century, when green verditer had come in and the azurite had not gone out of use. The other is the panel picture belonging to the collection of the late Mr. Hamilton Bruce, the original painting being dated with some exactness from the use of azurite, and of egg as the medium, and the subsequent re-painting being proved by the presence of oil as the medium, and its date approximately fixed by the high probability that the green used is Scheele's green.

In addition, the tendency was for an artist always to use the same palette, so that the use of smalt by Teniers, of blue verditer by Boucher, and of a mixture of verdigris and ultramarine by Watteau, is not without its importance when examining doubtful pictures supposed to be painted by these artists.

CHAPTER VIII.

ON THE MATERIALS USED FOR PREPARING MEDIUMS.

In the preceding chapters, the principal pigments used at various times in the history of art have been fully discussed, along with the study of actual examples. We shall now proceed to consider the information to be obtained from the study of mediums.

Before describing in detail the different substances which have been used as mediums, it is necessary to say a few words on the general history.

One of the earliest mediums of which we have existing records is beeswax, but there does not seem to be any authentic evidence of its use after very early times. At the same time it will be noted that in the description of illuminated manuscripts, I have detected one case of the use of beeswax in a late fifteenth century manuscript—a case which is of value as determining the date when oil of turpentine or some similar volatile medium was first used, and it may be that other cases exist, and that therefore the use of beeswax as a medium is worthy of further investigation.

The mediums therefore which we shall have to con-

sider can be divided into two great groups. The medium used by the tempera painters—egg—and the medium used by the painters in oil, consisting of drying oil such as linseed, nut, or poppy, either by itself or mixed with a varnish. Then, as we shall show, there is probably a third group in which both mediums are combined. It is unnecessary here to deal in detail with the historical evidence as to the use of these mediums. There can be no doubt that the use of egg as a medium has been customary from very early times. Pliny describes the use of white of egg for attaching gold leaf, and it is quite possible that egg was the medium of one school of Greek painters, while there can be no doubt that egg was the medium of the Mediæval painters, at any rate in Italy, up to about the close of the fifteenth century. The best account of the use of this medium is to be found in Cennino Cennini. Painting in oil is, however, also very early. There is no definite evidence that drying oils were used in Classical times, but the use of a drying oil on a varnish is described by Aetius in the sixth century, a receipt for an oil varnish is given in the Lucca Manuscript, and the properties of a drying oil as a medium for painting are described by Theophilus, while the account books at Ely and Westminster show the early use of oil in the thirteenth and fourteenth centuries.

One of the difficult problems in the early history of art is the question as to when wax was replaced by other methods of painting, and whether we are to regard the use of oil as a development from the use of wax. Wax is referred to as a medium in the Lucca

manuscript, but there is no reference to it at all in Theophilus, in which the mediums are egg and oil, so that it seems to have finally disappeared some time between the eighth and the twelfth centuries. There is also evidence from the discoveries made at St. Médard that in the north, at any rate, it was customary to mix the wax with pine balsams. The early oil varnishes also contain pine balsam as well as other resins, and we are consequently faced with the interesting speculation as to whether the history of mediums may not have been in the first place the use of wax, then mixing of wax with pine balsams, and the replacement of the wax by oil, so as to make an oil varnish, but there does not seem to be any definite evidence either from existing works of art or from manuscripts to clear up the obscure questions as to the mediums used before the twelfth century.

A matter of great importance is the problem of when what is now called "oil painting" was introduced. Egg, linseed oil and varnish are all referred to in the Ely and Westminster accounts, but this cannot be taken as finally clearing up the question as to the technique in the north. That the technique in Italy up to the middle of the fifteenth century was a pure egg technique, is sufficiently proved by the writings of Cennino Cennini, but we have no such clear and definite record of the methods used in the north, and it certainly is a matter of considerable doubt whether what we now call "oil" painting was used in the north before the close of the fifteenth century. These questions we shall have to discuss in more detail after discussing the mediums themselves.

Egg.—To begin then with Egg. Both the white and the yolk of egg have been used for painting, the evidence to be derived from Cennino Cennini being in favour of the yolk being the medium used for ordinary tempera work, while the white was rather used as the cement for attaching gold leaf. White of egg consists almost entirely of albumen, emulsified with water to the extent of 84·8 per cent. Albumen has the property, when heated or treated with certain reagents, of being coagulated into a solid, and if exposed in thin layers to the air, the same coagulation gradually takes place.

The yolk of egg, which is a more important medium for us to consider, consists principally of albumen, along with an allied substance Vitellin, an oil, and a compound called Lecithin, which has many of the properties of a fat. It may therefore be regarded from the point of view of the painter as an emulsion of albumen, water and fatty oil. This oil has the property of slowly hardening, although it cannot strictly be regarded as a drying oil, but apparently when mixed with a pigment and exposed in thin layers, the yolk of egg, owing to the slow drying of the oil, and coagulation of the albumen, sets into a firm hard medium, a medium which has proved to be very durable, judging by the length of time that tempera pictures have lasted.

Before leaving the question of egg, it is just worth while referring to the fact that in some of the receipts directions are given for stirring the egg medium with branches of the fig tree, and an interesting question arises on account of this, as the fig tree belongs to the family of the rubber trees, and has a milky juice which

apparently contains caoutchouc. It is not clear whether the intention is to actually add fig tree juice or not, nor, if it is to be added, the extent to which it is thought necessary, but the subject is worthy of further investigation, and experiments might well be made with mixtures of the exudations of rubber trees and yolk of egg, the properties of such a medium being compared with those of yolk of egg alone. For further information on this subject, the reader is referred to Mrs. Herringham's translation of Cennino Cennini, pages 184 and 212.

Beeswax.—A considerable number of waxes are known, but the only one of interest to us is ordinary beeswax which is a mixture of two substances—Myricin (myricyl palmitate), which is insoluble in alcohol, and Cerin, a substance which has been found to be a mixture of two fatty acids, while there is a small quantity of another substance still contained in the alcohol after cooling. It melts at 62-4° Centigrade, and can be bleached by exposure to air and sunlight. By long exposure to the air, it disintegrates, and partially perishes by oxidation, but must be regarded on the whole as a very durable and unalterable substance. It can be emulsified with oils, and forms a semi solution with spirits of turpentine and petroleum, which enables it to be used as a medium. After the drying off of the volatile medium, the surface can be polished with the hand or with a cloth, thus forming a continuous slightly shiny surface. It can also be emulsified with a little caustic soda or potash, and under this condition can be mixed with size or glue. Mediums of this kind are described in the Hermeneia

and in the manuscript of Jehan le Bèque, but there is no definite evidence that they have ever been used in the history of art.

Beeswax can be used directly as a medium if melted and laid on with the brush on a warm surface. Other experiments on this method of using beeswax will be found in "Greek and Roman Methods of Painting."

Linseed Oil.—Linseed oil is extracted from the seed of the common flax by grinding, warming and pressing, the finest samples of oil being, however, obtained by cold pressure from the seed. It is a compound of glycerine with fatty acids, the drying properties being due to the presence of linoleic acid. The important property of linseed oil from the point of view of the painter is the fact that it absorbs oxygen from the air and is converted into a substance called linoxine, this linoxine forming the leathery translucent skin with which we are familiar when linseed oil has dried.

The use of this word "drying" is unfortunate, as it gives an entirely false impression of what actually takes place during the hardening of linseed oil, the process being one of oxidation similar to the rusting of a piece of iron or steel. The rate of drying of linseed oil can be increased by boiling the oil, by which it is gradually thickened, and also by the introduction of what are known as dryers, the best known dryers being compounds of lead, such as white lead and litharge, and compounds of the metal manganese, such as manganese borate. Exposure to air and sun will also gradually thicken the oil and increase its rapidity in drying. Zinc sulphate is described as a dryer in some fifteenth and sixteenth century manuscripts.

It is questionable whether pure zinc sulphate has any such properties, but the crude zinc sulphate of that time seems to have contained a certain amount of manganese. Umber for the same reason acts as a dryer in linseed oil, owing to the presence of manganese in the pigment.

It is important, however, to note here that while such boiled oils are occasionally used by artists to hasten the process of drying, and are largely used by the house-painter, properly purified and sun-refined linseed oil does not require any artificial agents when ground with a pigment to make it dry. For instance, the ordinary artist's pigments are ground in a refined raw oil, and require no further treatment.

Poppy oil is obtained from the seed of the opium poppy, and is nearly of the same chemical composition as linseed oil, though it is a slower dryer. The preparation of this oil from the seed is mentioned by Dioscorides, but there is no account at this early date of its properties as a drying oil.

Nut oil is obtained from the kernels of the common walnut, and may be separated merely by boiling the peeled and crushed kernels with water, when the oil will settle on the top. It can also be obtained by pressure, and is very similar in constitution to linseed oil, but dries more slowly. The description of the preparation of this oil is found in Pliny, and there were other drying oils known, but these are the only ones which apparently were used in the early history of painting.

Turpentines.—Two varieties seem to have been used in Europe for the preparation of varnishes.

Venice turpentine, which is the semi-fluid resin obtained from the common larch, and consists of about 63 per cent. of resinous acids, 20 per cent. of terpenes, and 14 per cent. of resins. If spread out in a thin layer it very slowly dries into a hard resin, owing to the evaporation of the terpenes, and if heated the terpenes are rapidly given off, while if distilled they can be obtained as a volatile colourless liquid, similar in composition to what we now know as spirits or oil of turpentine.

Strasburg turpentine is the semi-fluid resin obtained from *Abies pectinata*, the silver fir, containing about 57 per cent. of resinous acids, 28 per cent. of terpenes, and 13 per cent. of resins. Strasburg turpentine is also known as Oleo di Abezzo, and in the same way loses its volatile constituents like Venice turpentine, leaving a hard resin. It is difficult to obtain commercially genuine specimens of either of these turpentines at the present time, but their physical and chemical properties are so closely represented by Canada balsam from the *Abies balsamea* that it can be substituted in most experiments in which it is necessary to test their properties.

These turpentines besides readily dissolving in alcohol, spirits of turpentine and linseed oil, are able to dissolve some of the harder resins such as amber and copal. If used for making a varnish, however, with a volatile medium, the resulting varnish is very easily destroyed, and becomes soft and sticky if slightly warmed. They have also the property, which has already been described, of dissolving copper acetate, forming a deep green varnish owing to the com-

bination of the copper with the resin acids to form resinates. They were largely used in Mediæval receipts for varnishes.

Mastic.—Among the many resins which are now known to commerce, there is only definite evidence of three having been used for the preparation of varnishes up to the close of the sixteenth century. The first of these is mastic. Mastic is derived from the *Pistacia lentiscus*, a tree growing in Scio and other islands in the Greek Archipelago. It occurs in small pea-like masses of a very pale straw colour, and can be crushed to powder between the fingers. It dissolves both in alcohol and in spirits of turpentine, and can also be dissolved in drying oils. It is largely used to-day for making picture varnish.

Sandarac.—The next resin is sandarac. In the older books this is described as the resin of the juniper, but what is now known as sandarac is obtained from *Callitris quadrivalvis*, a native of Algiers, and it is highly probable that the Mediæval sandarac was obtained from the same tree and that its description as being juniper resin is a mistake. It can be dissolved in oil of spike, and in several of the terpenes, but is only partially soluble in alcohol, and can be easily dissolved in drying oil to make a varnish.

Amber.—The third resin we have to refer to is amber. Amber is the most infusible of all the resins. It is a fossil resin and is found among other places along the shores of the Baltic Sea. It is only slightly soluble in the ordinary solvents, but after fusion can be dissolved in drying oils, the resulting varnishes

however, being very dark in colour, drying very slowly, and tending to flow more than the other oil varnishes. It is only by a very complex process that it is possible to get an amber varnish of a pale colour, and without entering into an elaborate discussion of the question, it is, I think, at any rate very doubtful if it is ever used as a varnish for painting purposes.

In addition to these three resins, it is quite possible that other resins came into the market during various periods in the history of painting, such as copal, for instance, but the whole description of the resins as given in the receipts is so obscure, that it is unwise to dogmatise as to what were the actual materials used in making Mediæval and later varnishes. The evidence as to the use of sandarac and mastic is fairly complete, but as I have already suggested, the evidence as to the use of amber is much more doubtful, as it is difficult to know whether the term would necessarily always refer to amber, or whether, as is quite possible, what was known as an amber varnish was so named from its colour, and not from its constituents.

Resin.—In conclusion, the residue left on heating the pine balsams so as to distil off the more volatile constituents, becomes what is now known as resin, and is referred to in the old receipts as Pica Greca. This substance dissolves readily in solvents such as alcohol and turpentine, and forms varnish which dries slowly and which becomes soft and sticky on warming, and has the property of the pine balsams already described of dissolving the harder resins and dissolving copper acetate. If, however, it is fused with copper acetate, the temperature rises too high and the verdigris is

decomposed. It is, therefore, necessary to dissolve it in a little spirits of turpentine before adding the verdigris.

Spirits or Oil of Turpentine.—As already stated, under the Turpentines, on distillation, a volatile liquid is obtained consisting of mixtures of terpenes which is known as spirits or oil of turpentine. The oil of turpentine used by painters at the present day is obtained from *Pinus Australis* and *Pinus taeda* and comes from America, but there is a French turpentine from *Pinus pinaster* and Russian turpentine from *Pinus sylvestris.* Spirits or oil of turpentine of the sixteenth century was no doubt of European origin, and therefore probably prepared from the larch or the silver pine.

On distilling these semi-liquid turpentines, with the assistance of steam, the volatile oil or spirits of turpentine comes over and is condensed. It will evaporate at ordinary temperatures. The boiling point varies a good deal according to the source and conditions of preparation. It is the solvent for beeswax, and for a considerable number of resins, and mixes readily with drying oils. On exposure to the air, it gradually absorbs oxygen and is converted into a sticky, resinous mass, so that old spirits of turpentine should not be used. As already described, when the semi-liquid turpentines are distilled with steam, the solid residue left behind is common resin or colophony.

Two other volatile mediums have been known since the sixteenth century to artists, *viz.*, petroleum and oil of spike. The native petroleum is a thick oil containing a series of products of various boiling points,

and is quite unsuitable for use as an artist's medium. It is found native in various parts of the world, including certain districts in Europe and Syria, so that the crude oil was known and described in classical times, but could not have been used for a medium unless subjected to some process of distillation.

By what is known as fractional distillation, it can be separated into different products of different boiling points. The petroleum used for artists' purposes boils below 170 degrees Centigrade. If a little drop is placed on a piece of blotting paper, it will evaporate and leave no stain. It is therefore a convenient medium for diluting, and can also be used for thinning varnishes, and many of the resins are soluble in it, just as they are in turpentine, so that spirit varnishes can be prepared from petroleum.

Oil of Spike.—Oil of Spike is the essential oil obtained by the distillation of *Lavandula spica.* It evaporates in the air, and readily absorbs resins, and has many of the useful properties therefore of spirits of turpentine for painting purposes. All these three volatile solvents are first mentioned in the sixteenth century receipts for the preparation of varnishes.

I do not propose here to go into an elaborate discussion either of the manufacture or properties of varnishes or the historical information as to their preparation. A great deal of information to be obtained from the old receipts must be regarded with considerable suspicion owing to the doubts which arise as to the correct names of the resins used. For our present purposes, it is only necessary to realise certain

broad facts as to the preparation and properties of varnishes.

Varnishes can be divided into two groups—oil and spirit varnishes. Spirit varnishes consist of a resin such as mastic or sandarac, dissolved in a volatile medium such as alcohol, spirits of turpentine, petroleum or oil of spike. On being painted out in a thin layer, the volatile medium evaporates and leaves a layer of the pure resin behind. Such varnishes are hard, brittle, and easily removed from the surface either by solvents or by mechanical injury. They have, however, the property of completely protecting from the attack of air and moisture, pigments which are mixed with them. Receipts for such varnishes occur in the sixteenth century manuscripts for the first time.

The other group of varnishes are known as oil varnishes, and are prepared by dissolving a resin in a drying oil. This can be done in the case of some of the softer resins by heating the oil and resin together for a sufficiently long time and at a sufficiently high temperature to result in the complete incorporation of the oil and resin with each other. In the case of the harder resins, such as copal and amber, it is necessary first to fuse the resin, then mix the oil with it and heat for some time until full incorporation has taken place, a simple test for this full incorporation being to allow a drop of the varnish to cool on a glass plate. If this cools to a clear drop, the heating has been carried sufficiently far. After dissolving the resin or resins in the oil, it is usual in the case of oil varnishes to add a certain quantity of spirits of turpentine in order to

thin the varnish and make it easier to use, but this is not essential, and it must be remembered, in the receipts for oil varnishes which are to be found in the fifteenth century and earlier, the only ingredients are the resins and the oil.

Modern oil varnishes are made principally from the harder resins such as copal, but in many of the old receipts we find a complex mixture of resins used, including the turpentines, such as Venice and Strasburg turpentine, while the amount of oil is much less than is customary in modern varnishes made from hard resins. Speaking roughly, the modern copal varnishes consist of about one-third of resins, two-thirds of oil, and one-third of spirits of turpentine, while the Mediæval varnishes consist of two-thirds of soft resins such as Venice turps, mastic resin, and sandarac, to one-third of oil. It is therefore thick and sticky and can only be used by warming and rubbing on with the hand.

Oil varnishes differ completely in their properties from spirit varnishes, owing to the fact that the final layer contains both drying oil and resin, thus producing a tough, hard, elastic surface. Owing to the presence of the oil, they share the properties of oil films of being permeable to water and gases, and therefore have not the same capacity for protecting pigments from chemical injury. The larger the resin content and the smaller the oil content, the better they act as protectors for pigments from chemical changes. The nature of the resin used does not seem to have any influence upon this result.

CHAPTER IX

THE METHODS OF EXAMINATION AND DETECTION OF MEDIUMS: HISTORICAL INFORMATION AS TO THE MEDIUMS USED.

HAVING briefly discussed the different substances which are used in the preparation of mediums, we shall next proceed to describe the methods by which they can be approximately identified in pictures.

In the first place the most important distinction to be made is between egg or size mediums and oil or varnish mediums, so as to be able to settle whether a picture is to be classified as an example of tempera or of oil painting.

For this purpose two methods can be used, which, to a certain extent, act as a check upon each other. If a tiny fragment of the pigment is moistened with cold strong sulphuric acid, it will be found that pigments that have been mixed with size or egg are not readily changed in colour. If, for instance, a little whitening is made up into a gesso with either size or egg and a fragment moistened with cold strong sulphuric acid, it will be found that while it readily dissolves, no change in colour takes place. If, on the other hand, it has

been mixed with an oil, varnish, or resin, a dark brown coloration is produced spreading into the liquid round the particle.

Another useful reaction is the use of methylene violet as a stain. If a solution of methylene violet and water of the strength used for staining is made up, and the section of the picture immersed in this stain, slightly warmed and kept in the stain for about half an hour, and then washed with alcohol, it will be found that in the case of egg and size, the particle is permanently stained violet, while in the case of oil or varnish, the stain is dissolved and washed away by the alcohol.

This staining method can be applied to the examination of an emulsion of egg or size with oil or varnish. I have made up with whitening and compared a large number of emulsions with mixtures of egg or size alone, and with oil or varnish alone, and I find that in the case of the emulsions they stain very lightly, but over the lightly stained surface may be seen under the microscope a certain number of dark spots where microscopic particles of egg or size have taken up the full amount of stain, this spotted appearance being therefore characteristic of a mixture of an oil varnish with egg or size. Such a mixture will, of course, also give the darkening with sulphuric acid which would not be given by the egg or size alone. It is as well to perform this staining both on a section containing the pigment and also, when the pigment can be removed by dilute acids, to dissolve out the pigment and then stain the medium left as a residue on the slide. The spotted staining should be found in both cases, while

where a layer of varnish, for instance, is lying over the under-painting, if the under-painting is either tempera or an emulsion, the thin transparent layer of unstained varnish will be clearly seen upon the slide above the region which has taken up the methylene violet stain.

The question might be asked as to whether, on an old picture, we have any right to assume that oil or varnish will behave towards reagents in the same way as a piece of modern paint. This is a difficult question to answer, but I have a certain amount of evidence to show that no marked change takes place in the chemical properties of these mediums under ordinary conditions. If, for instance, a perfectly obvious example of fifteenth century tempera work is taken, it takes up the stain just as readily, and in the same way as a modern piece of tempera painting, while if an obvious piece of oil or varnish painting is taken, say from a sixteenth century picture, it refuses to absorb the stain. Moreover I have made certain experiments to compare the condition of linseed oil on an old picture with the condition of linseed oil exposed to weathering out of doors. For this purpose I exposed a wooden panel, which was painted with zinc white, for some three or four years out of doors. At the end of that time, the paint was rapidly disintegrating, and being washed off by the rain. If a little particle of this disintegrated paint was placed under a microscope and treated with a weak acid, the zinc white dissolved, leaving the layer of dried oil behind. This layer of dried oil seemed to be quite homogeneous, and refused to take up the methylene violet stain. When, however, it was

attacked by a powerful reagent such as acetic anhydride, it was rapidly dissolved and disintegrated.

Acetic anhydride acts very slightly upon a recently dried film of linseed oil paint, and also very slightly on some fifteenth and sixteenth century paint films I have examined, so that I think we are justified in saying that linseed oil suffers greater chemical change in the course of three or four years' exposure out of doors, than it does in three or four hundred years upon the surface of a picture, and at the same time, that this exposed linseed oil is incapable of taking up the methylene violet stain, and we need not therefore fear the use of the stain to distinguish between oil and tempera pictures.

The impression I have formed from the examination of such exposed surfaces, is that there is really very little chemical change produced by weathering, and that the destruction of the paint is much more of the nature of a mechanical breaking up of the surface than of the change in the chemical properties of the linseed oil film itself.

A more difficult problem is to decide whether oil alone has been used to paint the surface, or whether a large proportion of varnish is present. I have made a very large number of experiments with different reactions with a view to getting something of a satisfactory nature for this purpose, trying, for instance, the effect of different strengths of cold strong sulphuric acid, and also a considerable number of the colour reactions which have been devised from time to time for the identification of resins.

The most useful reaction for detecting the presence

of a resin in oil is as follows :—Dissolve metallic tin in an excess of bromine and dilute the solution with about five volumes of carbon bisulphide; put a drop on the sample of varnish and allow it to evaporate to dryness in the air. This test is given in Allan's "Organic Analysis" (Vol. II, p. 463, 1886 edition) for detecting colophony, with which it produces a blackish-purple discoloration, but if an oil varnish is taken, owing, no doubt to the breaking up of the resin in its solution in the oil, it will be found that it reacts with this reagent.

A linseed film merely turns orange yellow, while copal varnish (containing about one-third copal to two-thirds of oil) turns reddish; mastic (containing two-thirds of resin to one-third of oil) turns still darker, while Canada balsam and colophony turn purplish-black. It is necessary, however, not to leave the dried particle too long exposed to the air, and experiments with this test should always be done with check samples. It is possible, if this is done, to decide whether oil alone, or oil mixed with varnish, has been used for painting a surface, and a very rough idea can be obtained as to the amount of varnish present.

I have so far not been able to obtain a satisfactory reaction for distinguishing between egg and size. This is, however, not a matter of very great practical importance, as we are pretty safe in assuming that the gesso on which a picture is painted will be made up of size, and the painting of the surface will be done with egg in the case of a tempera picture. The main problems that occur are solved by the reactions which I have already given.

Having now dealt with the experimental methods, I shall proceed next to consider in more detail the literary evidence as to the history of mediums.

The real problem which still remains to be finally settled is the nature of the medium which was used by Van Eyck and his immediate followers. There can be no question as to the use of tempera in Italy, or as to the use of oil in the modern sense, in the sixteenth century, though probably largely intermixed with varnish, but the appearance and state of preservation of the early Northern work certainly suggests that there was some peculiarity about the medium used at this time, and that it was neither oil on the one hand, nor egg on the other. It is necessary therefore to consider carefully what materials Van Eyck had to his hand for the preparation of mediums, and, after having considered these, to give such scant literary evidence as we possess.

The beautiful enamel-like surface and splendid preservation of Raphael's pictures make it also highly improbable that they were painted in oil colours.

As we have already seen, he had egg, and also oil, and he was no doubt quite familiar with the properties of drying oil, and, as I have shown, there is no need to suppose the discovery of special methods of preparing the oil, as has been suggested by Eastlake, as properly sun-refined linseed oil would meet all the practical needs of the painter.

In addition he had oil varnishes of the nature which I have already described, consisting of large quantities of fairly soluble resins dissolved in a comparatively

small quantity of linseed oil. I have prepared many such varnishes, and they are sticky and thick, and can only be applied successfully by warming and then rubbing on with the hand as is described by Cennino Cennini.

The next question is a very important one, and cannot be definitely answered, and it is whether he also had such volatile mediums as spirits of turpentine. As I have already explained, in order to prepare these volatile mediums, the art of distillation is necessary, and it is known that the art of distillation is very old, dating from somewhere about the second century. The alchemists were accustomed to distil various substances. Among these they early succeeded in preparing alcohol, and it is very likely may also have prepared such substances as spirits of turps. It is, however, one thing for a substance to be produced in the laboratory of the alchemist or the doctor, and another thing for it to be a commercial product which could be freely obtained and used by artists.

The first definite literary evidence that we have that these volatile substances were being used by painters is to be found in the sixteenth century manuscripts, where various receipts are given for preparing varnishes by dissolving resins in spirits of turpentine, oil of spike, and petroleum.

None of these volatile mediums are mentioned in earlier receipts, and this agrees fairly well with the date when alcohol first began to be prepared and sold in large quantities as a drink. It had long been known to doctors and alchemists, but it was at the close of the fifteenth century that the distillation of alcohol,

in commercial quantities, first took place, and it is highly probable that with the development of the commercial distillation of alcohol, the commercial distillation of these other volatile products first began.

In the descriptions of illuminated manuscripts, I have pointed out that the Speculum Vitæ Christi (18.1.7, Advocates' Library, Edinburgh), which we know to have been painted somewhere between 1465 and 1489, has been painted with a wax medium which could only have been laid on in such thin smooth coats by dissolving it in some volatile substance such as spirits of turpentine. This, as far as I am aware, is the earliest date at which the use of such a volatile medium has been proved in the history of art.

In discussing the transparent copper green, which was used from the eighth century on illuminated manuscripts, I have pointed out that the problem of its application is somewhat difficult, and that one possible solution is the use of spirits of turps, in which case we must suppose that spirits of turps was known and was in use for painting purposes in the monasteries from the eighth century, although there is no reference to it in any of the literary sources of information. But as far as my experiments go it was laid on with gum. On the whole, it is probably safer in the meantime to assume that, at the time of Van Eyck, turpentine was not known to artists, and that consequently we cannot regard this as one of the mediums which he had available for painting purposes. We are therefore driven to consider the possibilities of linseed oil, nut, or poppy oil, egg, and the Mediæval oil varnish.

There can have been no difficulty in painting

pictures either with egg or with oil, and if the condition of surface and preservation of the pictures of the time of Van Eyck corresponded with what we are familiar with in later genuine oil pictures, we should be quite safe in saying that they were painted in oil, but the remarkable preservation of these pictures, more especially the remarkable preservation of the medium in which they are painted, makes it difficult to believe that they are done in oil alone, while the amount of the Mediæval varnish that could be introduced into the oil would be very small indeed, without making the medium sticky and unworkable, and would be hardly enough to account for their fine preservation.

We have therefore to consider what other possibility remains. Let us suppose that the use of oil alone was not regarded as satisfactory owing to earlier experiments in oil having proved wanting in durability, and that the aim was to obtain a medium which should prove more durable either than oil or egg, especially under the conditions of a Northern climate. There remains only one other possibility, and that is the emulsifying of the sticky unworkable varnish with white or yolk of egg or a mixture of both, thus converting it into a material in which it is possible to grind pigments, and with which it is possible to paint.

We are then left with three possibilities—tempera painting, oil painting, and egg varnish emulsion painting. While of course there is always the possibility of a combination of these methods. It has, for instance, often been suggested that the Van Eyck pictures are really tempera pictures with glazings of transparent colour on the top. These glazings, if laid on with the

brush, cannot have been made in the Mediæval varnish medium, unless it was very much diluted with oil or emulsified with egg or copiously thinned with turps, so that whether we suppose the pictures to have been begun in tempera or not, the problem still remains as to the medium which was used for the finishing coats. As far as my experiments go I have found no confirmation of this view.

We shall now briefly deal with such literary evidence as exists on this question of mediums. I have already mentioned the fact that oil painting is described by Theophilus, and is also fully described by Cennino Cennini, and was evidently known in England as shown by the Ely and Westminster accounts. We want rather now to consider all the evidence there is as to the use of any other kind of medium. It is also unnecessary to quote again examples of Mediæval varnish receipts, and therefore we shall just discuss the evidence as to other kinds of medium.

References to emulsions are very few. In the notes in French by Jehan le Begue, at the end of his collection of manuscripts, we find two interesting references to mediums: one a medium (Mrs. Merrifield, Vol. I, p. 306) made out of wax and glue (a similar medium is described in the Hermeneia), and the other the statement that "All colours are distempered with the gum of the pine or of the sapin except minium or ceruse which are tempered with white of egg." (Mrs. Merrifield, p. 294, Vol. I.) This statement is obviously incomplete, as these liquids are quite unsuitable as mediums unless emulsified with egg or mixed with oil, or diluted very largely with spirits of turps. In the Strasburg Manu-

script, quoted by Eastlake, instructions are given to grind in oil and add a few drops of varnish to each, and in the Venetian Manuscript on which Herr Ernst Berger lays so much stress (Vol. III, p. 231) a medium is described for painting on glass consisting of the emulsion of egg and varnish.

The only other reference I know is the one given by Vasari, where in discussing the medium discovered by Van Eyck, he states that Baldovinetti and others tried emulsions of egg and varnish, but found that they cracked off.

In conclusion, it may be pointed out that the description given by Vasari of the Van Eyck medium certainly suggests that it was something more than linseed oil, and also that Vasari himself was not aware of its nature. It is also very evident that in Vasari's time the custom was merely to grind the pigments in oil with, at any rate in certain cases, the occasional addition of a little varnish, for he says—"Vanno poi macinando i colori con olio di noce o di seme di lino (benchè il noce è meglio, perchè ingialla meno), e così macinati con questi olii, che è la tempera loro, non bisogna altro, quanto a essi, che distenderli col pennello."

This is all the evidence which apparently exists as to the use of an emulsion medium, but it cannot be taken as proving that such a medium was not used, as the more that one investigates the history of pigments and mediums, the less confidence one has in the information to be obtained from literary sources. The existence, for instance, of the transparent copper green throughout the whole history of the painting of

illuminated manuscripts without a single reference to it in any of the books of receipts, is a remarkable instance of how little such collections of receipts are to be relied upon. No doubt if in the North, at the beginning of the fifteenth century, we had had an artist like Cennino Cennini, who wrote a complete description of the technical methods of his time, we should have had exact information as to the Van Eyck medium.

It also seems highly probable that whatever the Van Eyck medium may have been, it was not discovered by either of the brothers Van Eyck. It seems unlikely that they could have used with such absolute certainty a medium which they had experimentally evolved themselves, and it is much more probable that they were pursuing a Northern technique which reached its highest perfection in their hands, and which attracted the attention of Italian artists to its possibilities.

Probably much more significant in the history of painting methods was the preparation of these volatile liquids such as turps and petroleum, and their use for thinning varnishes and oil paint, thus solving the technical difficulties which had resulted in the emulsifying of egg with varnish, and leading rapidly to the practice of oil painting as we know it to-day.

I believe the first man to suggest that probably the Van Eyck medium was an egg varnish emulsion was Professor Ernst Berger. His interesting experiments on emulsions should be consulted.

I had myself independently been coming for many years to a similar conclusion.

CHAPTER X.

ON THE EXAMINATION OF THE MEDIUMS USED ON CERTAIN PICTURES.

Before describing the actual experiments on certain pictures, it is necessary to say something about the brilliant green which is found on the pictures by Van Eyck and his immediate followers, and also on some of the pictures by Titian and other fifteenth and early sixteenth century painters.

This green is not found in later works of art, and is of peculiarly fine quality, and has the appearance of being glazed over an underpainting. In the earlier chapters, the green prepared by dissolving copper acetate in a pine balsam has been described, and it has been shown that it was used on illuminated manuscripts through many centuries, only disappearing when we come to the fifteenth. Curiously enough, it is just at this time that we get this fine green appearing on "oil" paintings, and before the discovery of the existence of this resin copper green on illuminated manuscripts, I had already pointed out that it seemed highly probable that the Van Eyck green was prepared in this way.

The earliest receipt for its preparation, as I have already stated, is to be found in De Mayerne, but it may well have been in use before this time, and if the list of pigments available for painting in the fifteenth century is examined, and greens prepared by mixing the various blues and yellows, it will be found that they have no green which is able to match the Van Eyck green except the copper dissolved in resin.

In order to test this point, I prepared some of this green and gave it to Professor Baldwin Brown, who matched it against the greens found on the altar piece at Ghent. His report was that it was, if anything, not quite sufficiently brilliant, but very closely matched the greens to be found there.

The significance of the use of this green in deciding the nature of the Van Eyck medium is obvious, as its preparation involves the use of a pine balsam, and it would either have to be emulsified with egg, or mixed with a small amount of oil in order to make it practicable for painting purposes—in fact if only mixed with a little oil, it would probably be too sticky, so that its presence in the pictures certainly points to the preparation of a balsam or highly resinous varnish medium, and its emulsifying for painting purposes. I have not yet had the opportunity of obtaining an actual sample from a fifteenth century picture, so that the evidence as to its use is not so definite as in the case of the illuminated manuscripts, but the green occurs on a German panel in the National Gallery in Edinburgh, and I have examined it very carefully under the microscope.

If such a green is examined under the microscope,

it is very often seen to contain some bluish partially dissolved crystalline particles of verdigris, and in other cases small opaque brown spots where the verdigris has been over-heated and decomposed. The green on the German panel is much more of a grass green than that prepared from verdigris alone, but this difficulty is easily removed by adding a certain amount of saffron to the mixture which dissolves also in the pine balsam and so enables greens of various tints to be prepared. Saffron, under these conditions, would be absolutely permanent.

When the green on this German panel was examined under the microscope, it seemed to be remarkably transparent, and at the same time is evidently a green and not a mixture of blue and yellow. It is fairly well matched by sap green, but has quite a different appearance under the microscope, as sap green contains rich transparent brownish-green particles. The green on the German panel shows here and there bluish-green particles, and also here and there opaque dark brown particles. It is certainly not a mixture of blue and yellow, nor is it verdigris ground in oil, nor does it appear to be sap green, as if that had been used ground in oil, it would have faded long ago. Its whole appearance therefore agrees with the green prepared by dissolving verdigris in hot Venice or Strasburg turpentine. Moreover the surface shows that it has been laid on with the brush and not merely rubbed over as a smooth hot green varnish.

It is therefore probably diluted either with oil or turps, or emulsified with egg.

This therefore is the indirect evidence in proof of the use of highly resinous varnishes or balsams in early "oil" painting.

To consider next the direct evidence. The first example I had an opportunity of examining was from a series of panels in the Museum at Edinburgh, probably of German origin, which are obviously from the costumes of the fifteenth century, They have evidently never been in the hands of the restorer, but are in good preservation, except that they had been at some time mechanically injured and portions of the paint scraped off. This made it possible to secure a minute fragment of the paint at the edge of a large area of destruction. This fragment consisted of two layers—a lower layer of white lead which had been laid directly on the panel, and an upper layer of azurite blue. The lower layer consisted apparently of white lead in oil. The upper layer was covered with old varnish which had turned brownish-yellow and which may either have dated from the painting of the picture or been put on later. The azurite gave every indication of having been laid on with the egg varnish emulsion when tested with the method already described, of dyeing with methylene violet.

The next picture examined was the German panel in the National Gallery, Edinburgh, to which reference has already been made.

This also was quite typical in the quality of its surface and appearance, but had been laid over in recent times with a varnish. Under the frame at the edge, part of the paint had been broken away, making it possible to obtain a little isolated fragment—the

samples required, I may say, are not larger than a pin-head. This consisted of a yellowish thin chalk gesso, on which was laid a very thin painting which again was covered by a modern varnish. The conclusion come to by the tests was that the gesso medium and the painting medium were emulsions.

Here again the result of the examination under the microscope goes to show not only that the medium used for the gesso and for the painting was the same, but in both cases this was an emulsion of egg or size with oil or varnish. It will therefore be seen that the microscopic evidence given by these two fifteenth century "oil" pictures above described is in favour of the view that in both cases an emulsion was used. It would, of course, be necessary to examine a very much larger number of early oil pictures before a final conclusion could be come to as to the medium used, and therefore I do not wish to put too much weight upon two isolated experiments of this kind. I think, however, we are justified in saying, whether we regard the evidence from the green, or the evidence from the actual microscopic examination, that the probability in favour of the use of an emulsion by the early "oil" painters is considerably strengthened.

Such emulsions, in so far as I have had an opportunity of testing them, do not stand weathering out of doors as well as the pure oil or varnish. This, however, does not at all prove that they would not be very permanent if used for pictures which are kept indoors, as for instance, the egg medium which has proved so permanent would, of course, perish rapidly if exposed to weathering conditions. I have also noted a

tendency when dry to get covered with minute flaws when examined under the microscope. This does not always take place, and can probably be avoided, much of course depending upon the exact conditions under which the emulsion has been made up. It seems to me, therefore, highly probable that there was a tradition in the North for painting with an emulsion of egg and varnish which existed before the time of Van Eyck, and which was brought to its highest perfection by Van Eyck and his immediate followers. It is also possible that the rapid disappearance of this method and its replacement by the use of oil to which a little varnish had been added was due to the preparation in commercial quantities of the volatile mediums such as turpentine which opened up new possibilities to the artist in handling stiff and sticky mediums.

The next picture examined was from the collection of the late Mr. Hamilton Bruce, and is a portrait on panel which, judging by the costume, must have been painted about the close of the sixteenth century. We should expect then to find here a modified technique. The panel is in excellent condition, the medium in which it has been painted is smooth and hard, and when the thin coating of a modern varnish is removed, the surface beneath has got a slight egg-shell gloss and does not show any signs of deterioration.

The painting has been done on a thin layer of chalk gesso laid on the wood. Among the pigments used in painting the picture I found smalt mixed with white to produce the delicate grey of the ruff, and as we have already seen, smalt came into use in the latter

part of the sixteenth century, thus confirming the evidence obtained from the costume.

It will be noted that towards the edge of the picture some of the paint and gesso has been broken away, and I took advantage of this to remove some small samples of about the size of a pin's-head from this broken edge. If this broken portion had not existed one might similarly have taken tiny samples from the very edge of the panel, but there is more risk in that case that they may have been doctored up to repair accidental injuries. The result of the examination of these particles was to show that in the first place the oak panel had been covered with a stout coat of glue. Upon this had been laid a gesso which was not merely size and whitening, but also contained a certain amount of oil or varnish, thus being of the nature of an emulsion. On removing this gesso, a layer of paint was left which gave no indication of being itself an emulsion, and was certainly of the nature of an oil film, but on the application of special tests gave indications of the presence of varnish mixed in considerable quantity with the oil.

I have brought forward several reasons which I think make it at any rate highly probable that the Van Eyck medium was an emulsion of egg and varnish. If this view is correct, this present picture marks an interesting transition period from the Van Eyck medium to oil painting. The emulsion is no longer used in the actual paint, but it is used in the gesso ground, while in place of a mixture of egg and varnish we find a mixture in which the varnish probably contains more oil than would have been used

by Van Eyck, and, by the introduction of more oil and probably a certain amount of "turps," has been converted into a manageable medium.

In some tests which I made on a panel of a later date unfortunately the fragment that I had was so small that I cannot speak with certainty, but believe it to be oil alone on a gesso simply of whitening and size, thus corresponding with later practice. The results of this examination clear up completely, I think, the apparent difficulty of deciding when the Van Eyck medium was departed from and oil painting, as we know it to-day, came in. It is also of value in accounting for the magnificent state of preservation of many pictures of the sixteenth century, and, on the other hand, the decayed condition of others.

In the case of this particular panel the pigment and the medium have been perfectly preserved. There are one or two large cracks owing to the shrinking of the wood, and for the same reason there are fine longitudinal cracks running down the picture, but if the wood had been as durable as the medium, the picture would be as perfect as on the day on which it was painted. It is at present covered with a spirit varnish, and if this is removed the surface underneath is found to be extraordinarily hard, and with a slight, almost egg-shell gloss.

The hardness of the surface and the durability of the picture are easily understood if we consider the way in which it has been built up—the layer of glue passing to a mixture of glue and varnish in the gesso, and then the oil and varnish on the final surface, so that all is bound together by the similarity of the mediums.

The next point to be investigated was the perfection with which the high key of colouring of the face has been preserved. It is easy to see that the dark painting round the face is raised above the level of the face itself, but it seemed important to settle the thickness of these paint layers by actual measurement, and for this purpose a small sample was taken from the neck by means of a microscopic boring sampler which I have before described, and placed so that the edge could be examined. The result of this examination is distinctly interesting.

An ordinary layer of oil paint laid on flat with a brush upon canvas is from two to three-thousandths of an inch in thickness, and the paint on the neutral tinted background of this panel is about the same thickness, but the layer of white lead lying over the gesso on the neck is only about three ten-thousandths of an inch in thickness, or roughly one-tenth that of the rest of the picture. These very thin glazings are lying on cream-coloured gesso below, and it is easy, therefore, to understand why that part of the picture has remained so high in key.

It is of some interest to note in connection with these results that there is, I believe, a practice among picture-dealers when buying old Dutch pictures on panel, of testing them with the point of a pin. If the picture is hard right through, it is regarded as genuine, if it is merely hard on the surface, it is regarded as a modern forgery. It is easy to understand that where the technique which I have just described has been employed, the picture will be hard throughout. It is also of interest to note that the use of these emulsions

has not departed from the traditions of the workshop, as at the present day in the relining of pictures similar mixtures of glue and varnish are made use of.

The results of the examination of this picture seem to me to clear up many obscure points. Where this tradition had been kept to, the pictures are in perfect condition; where it had been departed from, the pictures have deteriorated; and gradually, as we move further and further from the time of Van Eyck, the tendency is to find pictures in worse and worse condition, while the passage from varnish and egg or size throughout the picture to varnish and size for the gesso and varnish and oil for the painting, and then from that to a gesso of size alone and painting with oil alone, are easy to understand.

I should therefore like to suggest, as opening up a new line of enquiry, that possibly the real revolution in methods of painting from the tempera of Italy and the egg-varnish emulsions of the North was due, not to any discovery in the possibilities of linseed oil, but to the preparation in commercial quantities of such mediums as turpentine and petroleum (we know, for instance, that Rubens used turpentine), and therefore it is rather to the history of the development of distillation as a commercial process that we have to look in order to get an explanation of the rapid change in technical methods which took place at the end of the fifteenth and beginning of the sixteenth century.

CHAPTER XI.

MICROPHOTOGRAPHY OF BRUSHWORK.

In the former chapters, the available information has been brought together on the history of pigments and mediums with the special object in view, as already explained, of assisting in the identification of works of art, and it remains now to consider another method which will enable us not only to say when a particular picture was painted, but also to identify the painter. This method has probably got its limitations, and it yet remains to be seen what these limitations are, but at any rate in a very large number of cases, it gives exact and valuable information.

If a picture is examined through a magnifying glass, it is possible to see the minute touches of the brush by which the artist has produced his effect, touches which are often beyond the limit of vision, although the highly-trained hand of the artist is able to place them quite accurately upon the canvas, but such an examination has obvious defects. It is capable, however, of being very much improved by using, instead of the ordinary lens, one of the stereoscopic magnifiers which

are now manufactured by Messrs. Zeiss, and which give a true magnification of the surface up to some three diameters, with much greater precision than is possible with the ordinary hand lens.

A great deal of very interesting information as to the methods used by a particular artist can be obtained by using these magnifiers made by Messrs. Zeiss. Here again, however, the method is defective, because in comparing two pictures with a view to deciding whether the brushwork has been done by the same hand, it is necessary to carry in the memory from one picture to the other, the complex subtleties of the painting—moreover, to a certain extent, the mind is influenced by the colour of the pigments, which tends to confuse the observation.

It is, however, quite possible to construct a camera with suitable lenses by which a small portion of the picture is thrown in a magnified form on the ground glass plate, and by suitable adjustments, this enlargement of the surface can be varied from one up to six diameters of the original. Moreover, by using one of the modern orthochromatic plates, the colour values are all corrected, and the resulting photograph gives an exact reproduction of the actual minute modelling of the surface of the paint. This photograph remains for comparison, and it is possible to put side by side photographs of two pictures for direct comparison into which no element enters except the brushwork. Even if a picture is painted on a large scale, and the brushwork is therefore comparatively coarse, this method will be found of value, although it may not be advisable to enlarge the brushwork on the negative at all, and

for this reason that it isolates the particular phenomenon we wish to study and the mind is no longer confused by the colour and the general form and balance of the picture. As far as my experience goes, a magnification of three diameters is the most useful for general cases. This amount of magnification is sufficient to bring out to the utmost and secure the minute details in the handling of the paint, while if the surface is magnified to a larger amount, this detail begins to disappear and mere masses of paint to be shown on the negative. If the magnification is carried to about this extent, the results obtained are very interesting.

The first experiments I made in this direction were on the well-known Watteau No. 55 (*a*) in the National Gallery, Edinburgh, and I selected one of the faces in the groups of figures for the purpose. The first result (*a'*), which is obvious, is the marvellous skill and accuracy with which the actual painting of the face had been done. The ear, for instance, which, in the original cannot have been more than one-eighth of an inch in length, is perfectly and accurately modelled by the brush, and might almost have been painted for a life-size portrait.

Another interesting result is the revelation of the way in which the face has been modelled up under the brush, the surface being almost mottled with complex touches of the brush, and doubtless owing to this process of modelling, giving a certain softness and richness of surface which one associates with the work done by Watteau.

The next photograph taken was of a very careful

copy of the picture by a good modern artist (Plate V)—a copy which was quite plausible when looked at in the ordinary way, but it will at once be seen on comparing this same face (Plate VII) that, apart from minute inaccuracies in drawing which are now made visible, and which are not visible without magnification, the whole handling of the brushwork is completely different, and is obviously weak and inefficient. The artist has not known what the point of his brush was doing, and what he intended the point of his brush to do when it was laying on the paint with the precision that we find in the case of Watteau. It is only necessary to compare these two photographs to realise by how completely different a method the copyist has produced a plausible imitation of the original.

The next photograph taken was of a face (Plate IX) from a picture by Pater (Plate VIII) which is also in the National Gallery of Edinburgh (No. 60). It seemed of interest to see how far Watteau's methods could be traced in his most successful pupil. Here again, if the photograph is examined, there is the revelation of a completely different handling. The work is accurate, and shows that the artist was a master over his brush, and knew exactly how to produce his effects, while in the way in which the eyes and mouth are produced, the influence of Watteau is quite obvious. On the other hand, in place of the rich and subtle brushwork that we find in Watteau's face, we have a very obvious and easy method of producing the required effect, the paint being laid smoothly on the face and then modelled up with one or two obvious shadows.

These three photographs then, at once reveal the

possibilities of this method, and bring into sharp contrast the work of a great master like Watteau, the work of a successful and facile painter like Pater, and the work of the copyist. They are also interesting as a revelation of the way in which Watteau produced those soft and rich effects which are associated with his work.

Having thus illustrated the kind of information that can be obtained, the next two or three photographs are selected with a view to giving a general impression of the methods of painting made use of at different times. The first one is a portion of the beard in one of the figures in the Mabuse in the National Gallery, London (No. 2790) (Plate X), and is a sample of very highly finished work, which we associate with the name of Van Eyck and his followers. It does not matter how much the surface is magnified, no indications of brushwork appear in this early work, but, at the same time, the result of the magnification is to bring out the almost microscopic accuracy of detail and finish which would be very unlikely to occur in the work of a forger or an inferior hand.

The next photograph is taken from Raphael, No. 744 (Plate XI), National Gallery, London, and is the foot of the infant Christ, magnified some $2\frac{1}{2}$ to 3 diameters. In Raphael and the men of his School we also get very high finish of surface, and the actual brushwork is concealed. At the same time, an enlarged photograph like this brings out both the detail and the perfection of the drawing, and therefore should prove of value in the identification of pictures by real masters of that time.

The real power of the method, however, is to be found later on, when artists begin to show their brushwork, and as an illustration of this I give a photograph of the eye in the Rembrandt, No. 755 (Plate XII), N.G., magnified to the same extent. I have in this way carefully compared the eye of some of the great Portrait Painters, such as Rembrandt, Van Dyck, Franz Hals, and find in every case the handling is quite different. In the case of life-size portraits there can be no doubt that the eye and the mouth are probably most instructive.

The next examples I propose to take are to illustrate actual problems into which I have made an enquiry by means of this method. The first is into the authenticity of a Teniers in a private collection.

The next photograph was taken from the Teniers No. 25 (Plate XIII) in the National Gallery, Edinburgh.

The first microphotograph (Plate XIV) is of the head in No. 25 of the peasant drinking. It is of great interest as showing the method used by Teniers at the date at which this picture was painted for modelling up a face.

The actual brushwork on this face is not quite obvious at once, on account of the somewhat high finish, and it is necessary to look at a piece of Teniers' later work in order to grasp his method. I therefore next reproduce the head of the old servant in the picture in the National Gallery, London, No. 817 (Plate XV). If this head is still further magnified by looking at it through an ordinary hand magnifying glass, it will be seen that the brush work consists of short, broad, straight strokes, with here and there in

addition, very fine lines slightly curved, for producing the hair on the beard, and so on. If now the peasant's head, already referred to, is examined through a magnifying glass, it will be found that the brush work is essentially the same, so that while Teniers modified very much the external character of his work, his method of laying on paint did not alter.

The next photograph (Plate XVI) is the head of an old man appearing in a picture in a private collection, which was under examination to see if it was genuine, and which is here reproduced by the kind permission of the owner of the picture. The model is evidently the same, and therefore the picture is most probably either painted in Teniers' studio, or is a forgery, the old man having been copied from a genuine Teniers. If the magnifying glass is applied to this head, it will be found that, while there are certain touches here and there closely resembling Teniers, the actual modelling up of the face is done by a completely different method, and therefore this picture has either been painted in his studio and touched up and signed by the master, or is a forgery, but it is not the work of the master himself.

The next microphotograph (Plate XVII) is taken from the back of the peasant in No. 25 and shows at once that in this case some restorer's hand has been at work as the modelling with the brush is quite different from and vastly inferior to that shown in the other two photographs.

The next problem which is illustrated here is the one of who painted "The Old Gray Hunter" (Plate XVIII) in the National Gallery, London.

The reason for taking these photographs was the statement by Dr. Bredius that "The Old Gray Hunter" was a picture by Verbeecq and not by Paul Potter at all. I began therefore by taking a microphotograph of the head of the horse in "The Old Gray Hunter" (No. 1009) (Plate XIX), and the head of a cow in the Paul Potter, No. 849 (Plate XX). These microphotographs, when compared, show at once, I think, that the brushwork of the horse, though in some ways similar, is very inferior to the brushwork of the cow—which looks much more like the work of a master hand. So far, therefore, they confirm the views of Dr. Bredius. My next step was to take a microphotograph of an authentic Verbeecq in the Gallery at The Hague. I took a microphotograph of the horse's head (Plate XXI) and also of the man (Plate XXII) on the horse's back. On looking at the horse from the Verbeecq it is quite evident that the brushwork is entirely different from that of the horse in "The Old Gray Hunter." When I pointed this out to Dr. Bredius, he suggested that I should take a photograph also of the sleeping man in the corner of "The Old Gray Hunter" (Plate XXIII). If now, the photograph of the sleeping man in "The Old Gray Hunter" and the photograph of the horse and the photograph of the man—both from the Verbeecq—are compared, it is, I think, at once obvious that all these are by the same hand; and that there can be no doubt therefore that the picture in the National Gallery was originally a Verbeecq. But it remains very difficult to account for the brushwork of the horse in the picture.

If now the picture itself be re-examined, it seems to me fairly obvious that the horse is an addition, and

does not belong to the original design of the picture. It is not in true perspective, and the bridle is really far in front of the hand of the sleeper in which it is lying; while the hand of the sleeper is not in an impossible position quite apart from the presence of the bridle. It is, of course, possible that the horse is by Paul Potter, and that the artists have collaborated in producing a picture, but in that case the inferiority of the brushwork to Paul Potter's has to be explained. The most probable explanation is, I think, that the picture has originally been by Verbeecq and that the horse is an addition by another hand. The general modelling of the horse, apart from the brushwork, suggests Verbeecq, and it is possible, therefore, that the original picture contained a horse by Verbeecq which has been re-painted, or that the artist who painted the horse had a Verbeecq horse in front of him. It is difficult to understand why a horse should be introduced at all, as the men are out with dogs and guns. Probably a microscopic examination of the picture would throw further light on it, as it would enable us to tell whether the painting of the horse was at a later date from the rest of the picture. There are apparent indications of re-painting on parts of the background under the belly and other parts of the horse.

But I think that these photographs have established, in the first instance, that the original picture is by Verbeecq, and that the horse is by another hand,—and that it is highly improbable that that other hand is Paul Potter's. I have compared the microphotograph of the cow No. 849 with a microphotograph of a cow

in a pedigree picture at The Hague, and the brushwork is exactly the same, thus establishing the authenticity of No. 849.

The next examples of problems are taken from the two pictures in the National Gallery—the portrait of Philip IV. by Velasquez, known as the "silver portrait," No. 1129, the portion selected being the tassel on the leg (Plate XXIV), and the other photograph is taken from the tassel on the leg of "The Spanish Admiral" (No. 1315) (Plate XXV). As is known, Beruete has thrown doubt on "The Spanish Admiral" being by the hand of Velasquez. It seems to me that if the brushwork of these two portions be compared, there can be little hesitation in saying that they are both by the same hand, and therefore if the "Philip" is to be regarded as an authentic picture there can be no question about the authenticity of "The Spanish Admiral."

In each case we must select from the picture something that will be characteristic of the particular painter's work. In the case of pictures with small figures in them, we cannot do better than select the face; in the case of large portraits, a photograph of the eye and the mouth will be found useful, as it is there we shall probably find the most subtle details of the brushwork of the artist.

In the case of landscape painters, the foliage of trees is specially worthy of study. As will be shown by the photographs next to be discussed, every artist has his own method of reproducing foliage, and these methods vary to an extraordinary extent in their complexity and subtlety of detail.

In order to show the characteristic methods of producing foliage I have selected two or three examples from many photographs which I have taken in the different galleries.

The first is from Pijnaker (Plate XXVI) and is a good example of the orthodox painting of foliage to be found in the Dutch School of Painting. The next example from Hobbema (Plate XXVII) shows a much more complex and individualised handling of foliage. The next example is taken from Crome (Plate XXVIII) and Constable (Plate XXIX). They are very interesting as showing the development of the treatment of foliage at a later date. For comparison with these and with one another I give examples from the modern schools, namely, the painting of the branches of a willow tree by Corot (Plate XXX); the painting of a poplar by Courbet (Plate XXXI); and the painting of foliage by William Maris (Plate XXXII) and by Troyon (Plate XXXIII).

The few examples which I have selected from many microphotographs which I have taken are sufficient, I think, to show the importance of this method as assisting in the identification of works of Art. It is too early to say exactly what its limitations are. It is questionable whether it will be of much value for the typical Italian sixteenth century picture, in which the methods of painting were more or less stereotyped, and the brushwork largely concealed. It is, at any rate, better to apply it, in the first instance, until more experience has been obtained, to pictures belonging to the later period, when brushwork was shown ; and there can be no doubt of its power when dealing with

pictures containing fine painting and small figures, such as Teniers and Watteau, and the Landscape painters when applied to the problem of foliage.

It has thus a very large field of application, and it remains to be seen how far these boundaries can be extended by experience.

When two pieces of brushwork are found to be the same, there is no need, of course, to enquire further into the matter, but where the brushwork on a supposed authentic picture is found to be different, it would be unfair to judge by one example, and it would be necessary to collect authentic examples of the painter's work at different periods in his career, the problem at once becoming more complicated. But by degrees one should collect a complete dossier for every important painter from carefully authenticated works of Art, which would remain for reference when a doubtful work came into the market.

In conclusion, it will be seen how closely connected the two parts of this book really are. In both cases, exact scientific methods are brought to bear upon the problem of dating and identifying a picture, and they should both be utilised,—and while not for a moment replacing the judgment of the Art Expert, they should be of very great assistance to him when forming a conclusion.

CHRONOLOGICAL LIST OF MANUSCRIPTS EXAMINED.

Page.	Century.	GENERAL ILLUMINATED MSS.	Place.	Date.
62	7	Add. 5111. pp. 10. 11. Fragment of Gospel Book ...	Brit. Mus. ...	6th or 7th cent.
70	8	Nero D. IV. Lindisfarne Gospels	,, ...	700.
77		Vesp. A. I. Canterbury Psalter	,, ...	
80		1 E. VI. Canterbury Gospels	,, ...	Late 8th cent.
96	9	Harley 2788. Codex Aureus	,, ...	800.
65	10	Arundel 547. Gospels	,, ...	Early 10th cent.
65		Add. 28815. Gospels, &c.	,, ...	
84		Vesp. A. VIII. King Edgar's Charter to Winchester	,, ...	966.
85		Galba A. XVIII. Athelstane's Psalter	,, ...	Mid. 10th cent.
107	11	Laing 5. German Gospels	Ed. Un. Lib.	
74		A. Ca. 44. Irish Psalter	,, ...	
85		Arundel 155. Canterbury Psalter	Brit. Mus. ...	1012–23.
86		,, 60. Winchester Psalter...	,, ...	1060.
65		Add. 19352. Psalter...	,, ...	1066.
66		Add. 11870. Metaphrastes...	,, ...	11th–12th cent.
104		30337. Exultet Roll	,, ...	End of 11th cent.
76		Add. 36928. Psalter...	,, ...	,,
66	12	Egerton 1139. Queen Melissenda's Psalter, fol. 1–12 b	,, ...	1131–44.
		,, ,, ,, ,, ,, fol. 202–11	,, ...	
67		Harley 1810. Gospels	,, ...	Mid. 12th cent.
86		Nero C. IV. Winchester Psalter...	,, ...	1160.
87		18. 2. 4. Rochester MS. Serm. de Temp.	Ad. Lib. Ed.	
87		6 C. VIII. Orosius, from Rivaulx Abbey	Brit. Mus. ...	Late 12th cent.
104		18859. Monte Cassino Psalter	,, ...	
88		2 A. XXII. Westminster Psalter	,, ...	End of 12th cent.
104		9350. Italian Psalter	,, ...	,,
	13	17742. Amiens Missal	,, ...	1218.
89		1 D. X. English Psalter	,, ...	Before 1220.
106		2 B. III. Flemish Psalter	,, ...	Mid. 13th cent.
		Add. 17868. French Psalter	,, ...	1260.
89		3 D. VI. Petrus Comestor...	,, ...	1283.
67		Burney 20. Gospels	,, ...	1285.
		28162. Somme le Roy	,, ...	About 1300.
91		Egerton 1151. Horae	,, ...	13th cent.
91		"Ruskin Bible"	Ad. Lib. Ed.	,,
91		18. 2. 13a. Hyrdmanniston Breviary (Northern) ...	,, ...	,,
92		18. 1. 2. "St. Giles Bible"	,, ...	,,
105		10. 1. 4. Justinian's Institutes	,, ...	,,
108		Add. 17687. Life of Christ...	Brit. Mus. ...	,,
66		Add. 36929. Psalter	,, ...	,,
76		18. 5. 19. "Rosslyn Missal"	Ad. Lib. Ed.	,,
92	14	Arundel 83. East Anglian Psalter	Brit. Mus. ...	Early 14th cent.
68		Add. 11838. Gospels	,, ...	1326.
92		Luttrell Psalter. East Anglian	,, ...	1340.
		19 D. II. Poitiers Bible	,, ...	Before 1356.
		17 E. VII. Bible Historiale	,, ...	1357.
105		Add. 21965. Tailors' Guild, Perugia	,, ...	1368.
93		18. 6. 5. Psalter of Eleanor de Bohun	Ad. Lib. Ed.	1382–99.
93		Add. 29704. Missal	Brit. Mus. ...	End of 14th cent.

Page.	Century.	GENERAL ILLUMINATED MSS. (*Continued.*)	Place.	Date.
105	15	Add. 22497. Dyers and Quiltmakers' Guild, Perugia	Brit. Mus.	Before 1403.
		Harley 2897. Burgundy Breviary	,,	,, 1419.
103		Dom. A. XVII. Henry VI Psalter	,,	1430.
103		Add. 35312. Horae	,,	Mid. 15th cent.
105		Add. 14802. Florentine Missal	,,	1457.
95		18. 1. 7. Speculum Vitae Christi (wax medium)	Ad. Lib. Ed.	1465–89.
107		18. 7. 18. Horae	,,	15th cent.
103		18. 8. 13. Horae	,,	,,
118	17	33572	Brit. Mus.	1661.
118		22494	,,	1686.

Page.	Century.	VENETIAN DUCALI.	Place.	Date.
106	15	Add. 21463	Brit. Mus.	1486.
113	16	20916	,,	1501–21.
115		18000	,,	1521.
116		15518	,,	1531.
106		Egerton 754	,,	1534.
106, 116		,, 755	,,	1538.
116		17373	,,	1554.
116		Kings 156	,,	1568.
116		16996	,,	1587.
116	17	23970	,,	About 1603 (1595–1605)
116		17348	,,	1613.
116		17349	,,	1613.
117		Eg. 759	,,	1635.
117		Eg. 760	,,	1643.
117		Eg. 761	,,	1644.
117		15131	,,	1647.
117	18	15140	,,	1700.

Page.	Century.	CORAM REGE ROLLS.	Place.	Date.
119	16	1013	Record Office	1515.
120		1012	,,	1515.
120		1126	,,	1543.
121		1185	,,	1558.
121	17	1450	,,	1616.
122		1499	,,	1621.
122		1562	,,	1629.
122		1537	,,	1625.
122		1826	,,	1672.

INDEX

NOTE.—In the case of important pigments to which there are many references, the more important references are printed in bold figures.

R. CLAY AND SONS, LTD., BRUNSWICK ST., STAMFORD ST., S.E., AND BUNGAY, SUFFOLK.

Plate IV. Picture by J. A. Watteau.
(no. 55) National Gallery, Edinburgh.

Plate V. Copy of Picture by J. A. Watteau. (no. 55)

Plate VI. A Head in picture by J. A. Watteau.
National Gallery, Edinburgh. (No. 55).

Plate VII. Head in a copy of a picture by J. A. Watteau.

Plate VIII. Picture by Jean Baptiste Joseph Pater.

(no. 60) National Gallery, Edinburgh.

Plate IX. Face from a picture by Jean Baptiste Joseph Pater.

National Gallery, Edinburgh. (No. 60).

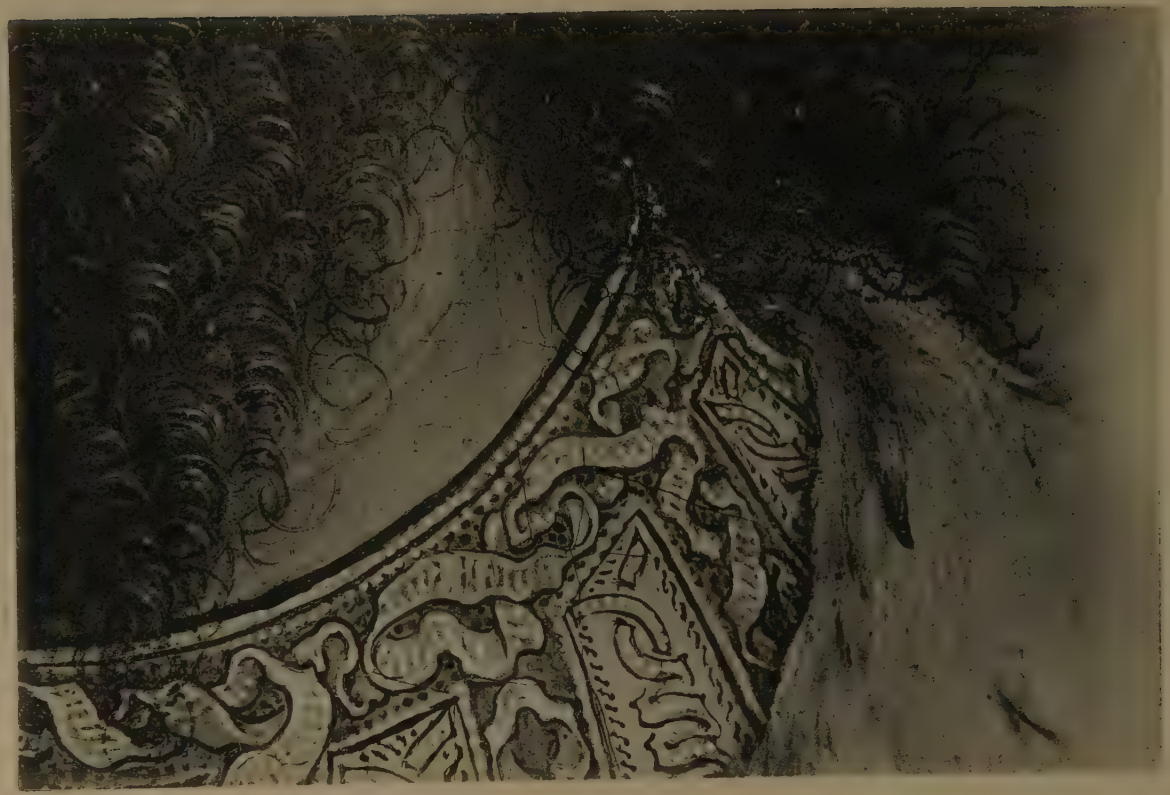


Plate X. Portion of beard in one of the figures in picture by Jan van Mabuse. National Gallery, London. (No. 2790).

Plate XI. Foot of the infant Christ, from a picture by Raphael. National Gallery, London. (No. 744).

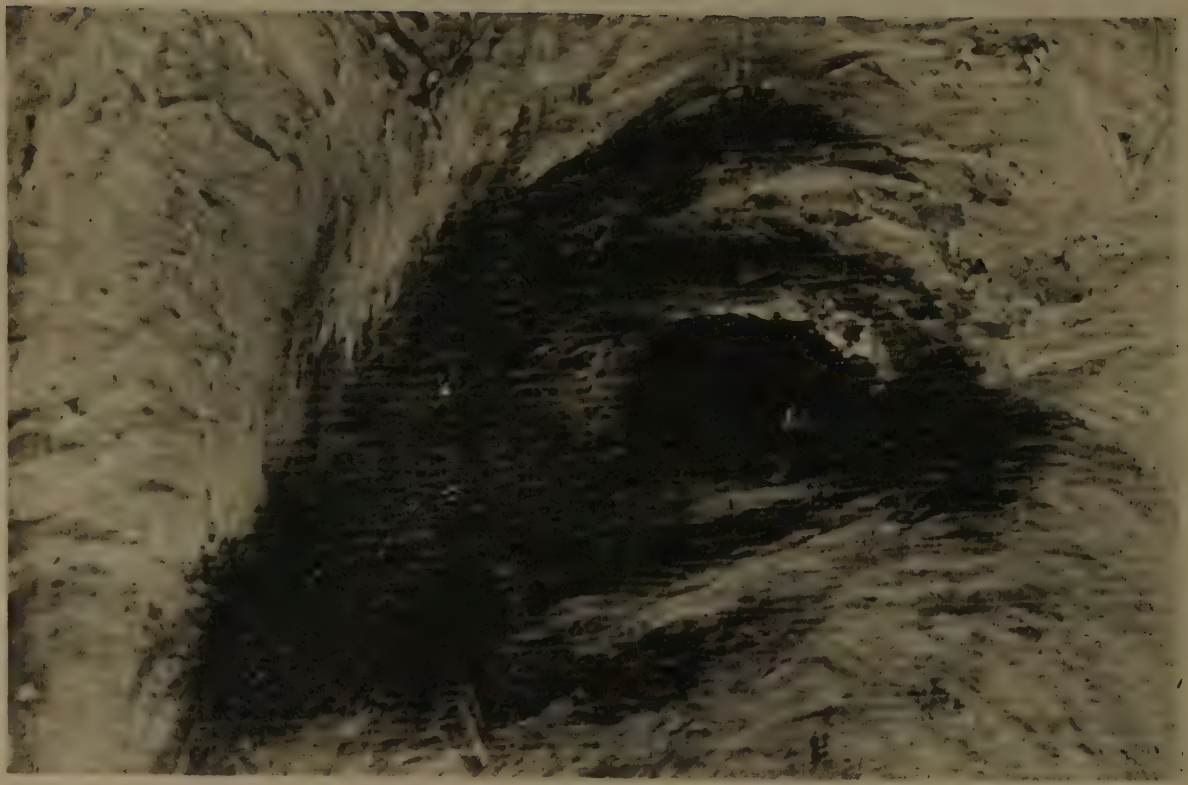


Plate XII. Eye in picture by Rembrandt H. van Rijn.
National Gallery, London. (No. 755).

Plate XIII. Dutch Boers Drinking, by David Teniers the Younger (no. 25) National Gallery, Edinburgh.

Plate XIV. Head of a peasant drinking, in a picture by David Teniers the Younger. National Gallery, Edinburgh. (No. 25).

Plate XV. Head of the old servant in picture by David Teniers the Younger.
National Gallery London (No. 817).

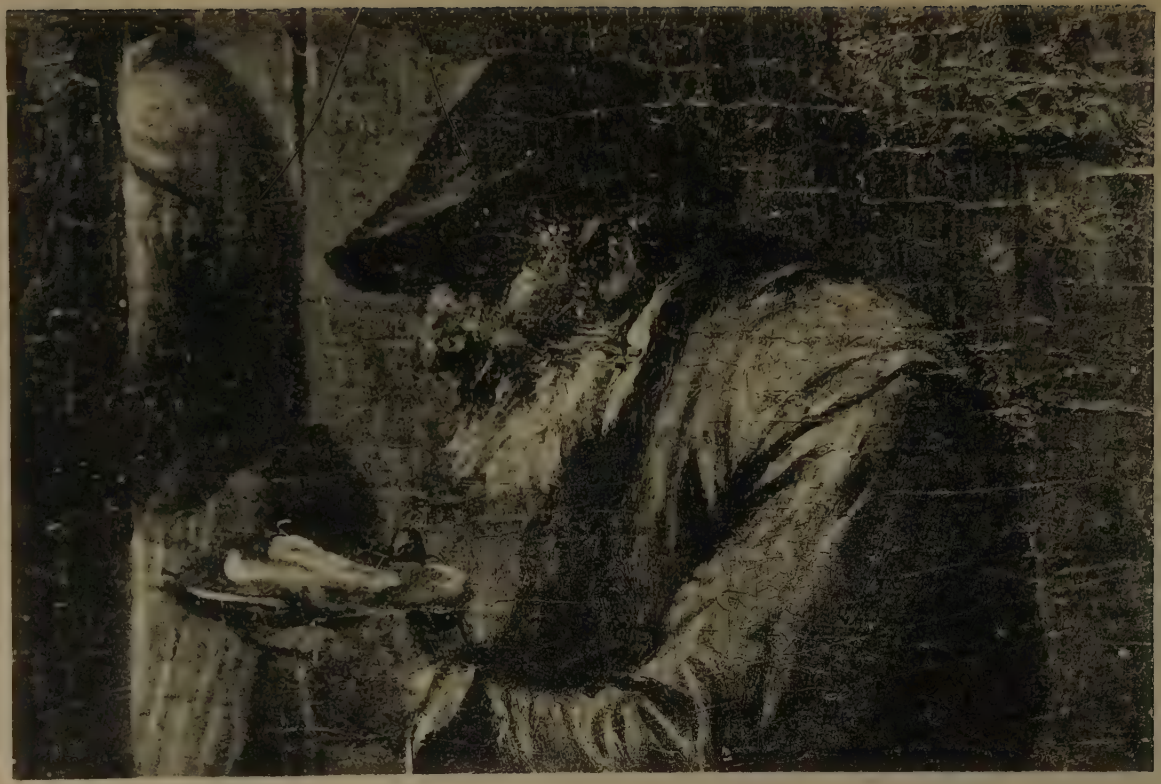


Plate XVI. Head of an old man in a picture in a private collection supposed to be by David Teniers the Younger.

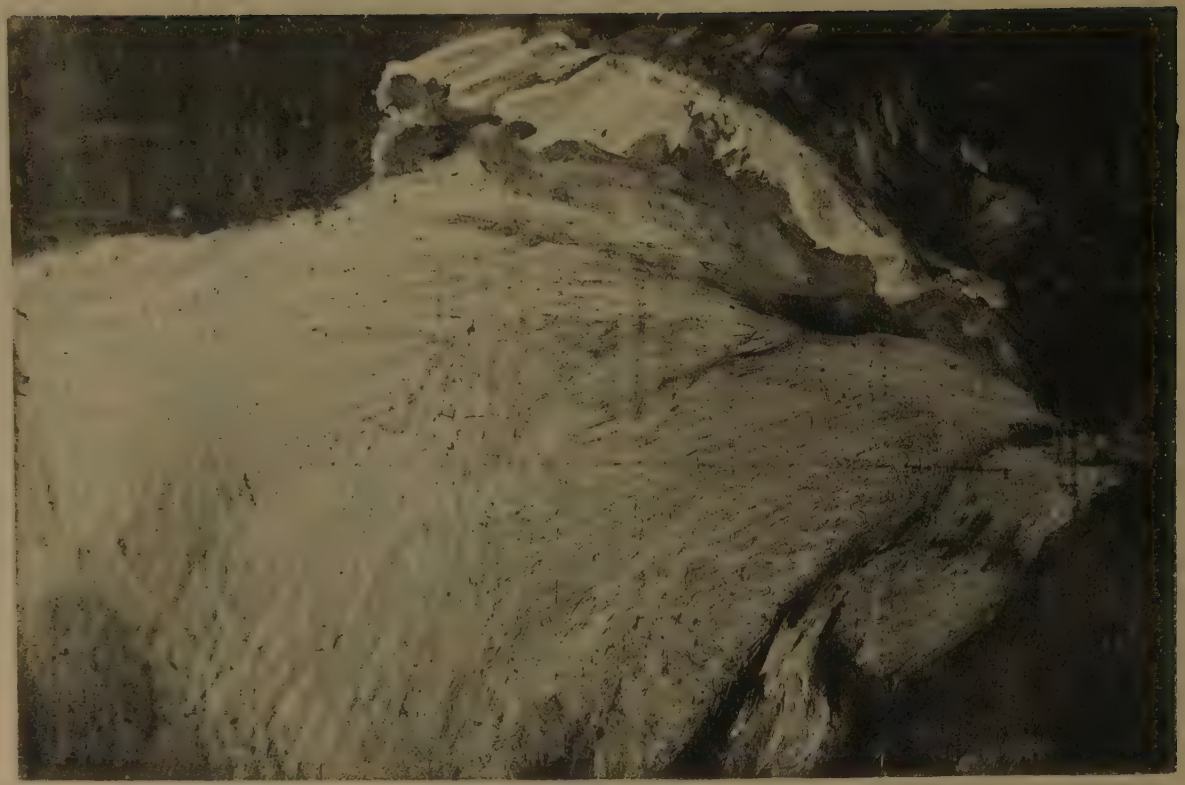


Plate XVII. Back of peasant in picture by David Teniers the Younger.
National Gallery, Edinburgh. (No. 25).

Plate XVIII. "The Old Gray Hunter."
National Gallery, London. (No. 1009).

Plate XIX. Head of horse in "The Old Gray Hunter".
National Gallery, London. (No. 1009).

Plate XX. Head of cow in a picture by Paul Potter.
National Gallery London. (No. 849).

Plate XXI. Horse's head in a picture by Pieter Cornelisz Verbeecq, "Two horsemen near a brook." Mauritshuis Gallery, The Hague.

Plate XXII. Man on horse's back in picture by Pieter C. Verbeecq, "Two horsemen near a brook." Mauritshuis Gallery, The Hague.

Plate XXIII. Sleeping man in corner of "The Old Gray Hunter".
National Gallery, London. (No. 1009).

Plate XXIV. Tassel on leg, Philip IV. by Diego R.D.S.Y. Velazquez.
National Gallery, London. (No. 1129).

Plate XXV. Tassel on the leg of "The Spanish Admiral."
National Gallery, London. (No. 1315).

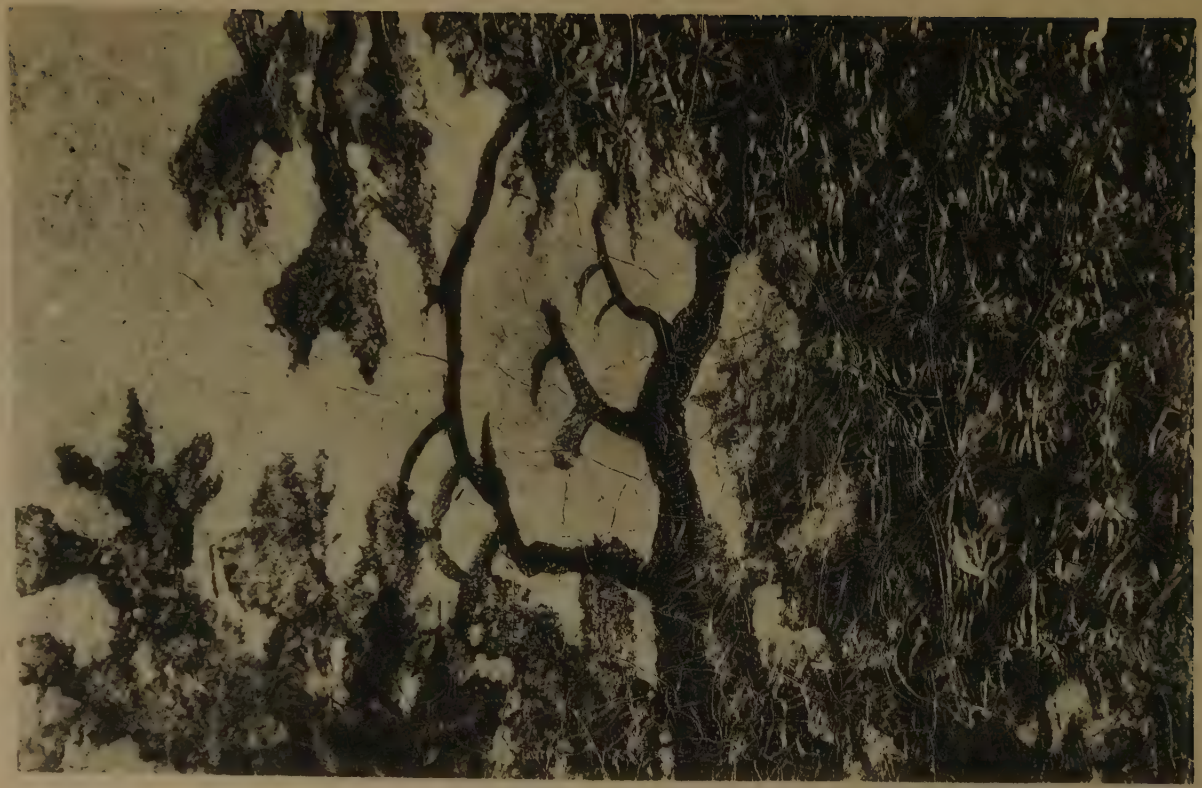


Plate XXVI. To show Adam Pijnaker's method of producing Foliage.
From a picture in the National Gallery, Edinburgh.

Plate XXVII. To show Meindert Hobbema's method of producing foliage. From a picture in the National Gallery, Edinburgh.

Plate XXVIII. To show John Crome's method of producing Foliage.

From a picture in the National Gallery, Edinburgh.

Plate XXIX. To show John Constable's method of producing foliage.

From a picture in the National Gallery, London.

Plate XXX. Branches of a Willow Tree by Jean Baptiste C. Corot, from a picture in the National Gallery, Edinburgh.

Plate XXXI. From a painting of a poplar by Gustave Courbet.
From a picture in the National Gallery, Edinburgh.

Plate XXXII. Painting of foliage by William Maris.
From a picture in the National Gallery, Edinburgh.

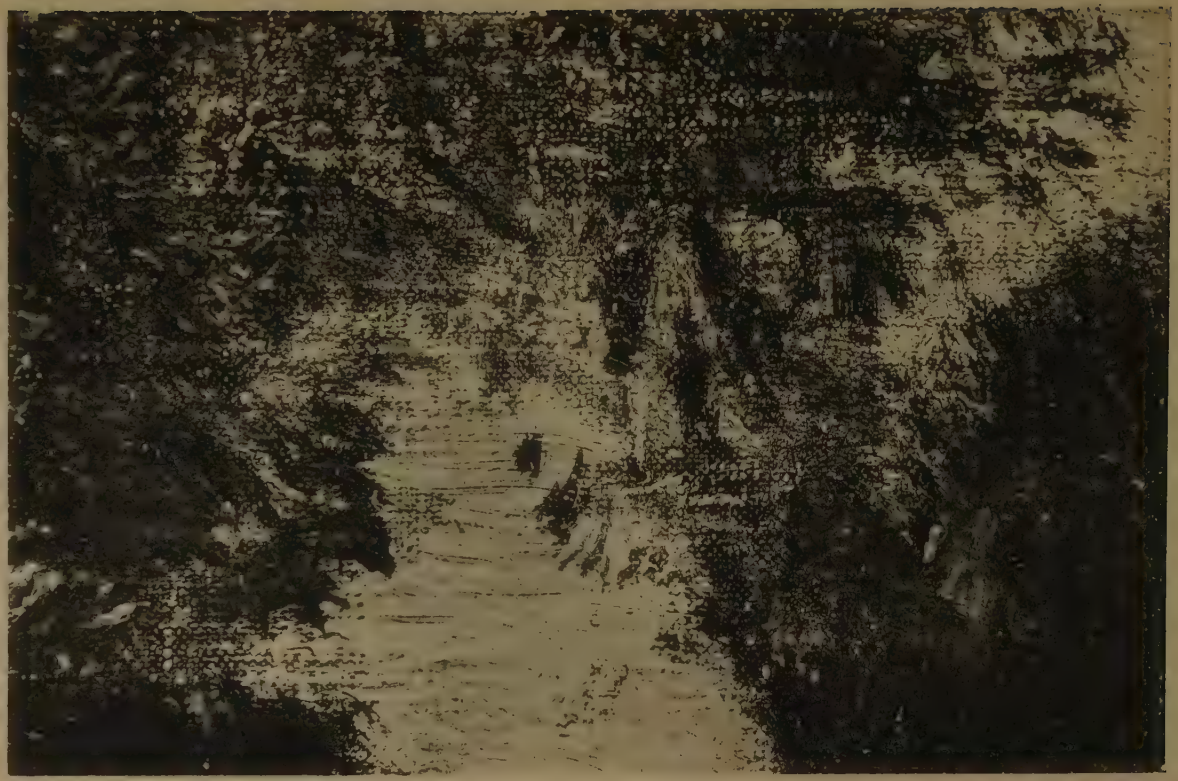


Plate XXXIII. Painting of foliage by Constant Troyon,
(From a picture in the National Gallery, Edinburgh).

Plate XXXIV. Horse's head in a picture by Philip Wouwerman, Rijks Museum, Amsterdam.